

# Interaction of Polymers and Mechanical Waves

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*New techniques of Mason, McSkimin, Hopkins and co-workers for generation of shear waves over the frequency range  $2 \times 10^2$  to  $2.4 \times 10^7$  cps have been used to study mechanical properties of chain polymers. Polymer solids, melts and dilute solutions, representing the main states in which plastics and rubbers are fabricated or used, were explored to find the characteristic relaxation times, rigidities and viscosities of various chemical structures. Polyisobutylene, hevea rubber, polydimethyl siloxane, vinyl chloride-acetate copolymers and plasticized nitrocellulose were compared with polyethylene and polyamides as examples of the range of solid properties encountered.*

*As melts, several polyisobutylenes, polybutadiene, polypropylene, polypropylene sebacate and poly- $\alpha$ -methyl styrene were investigated as models for varying degrees of chain substitution. Chain rigidity in, for instance, polyisobutylene, seemed to reflect visco-elastic over-all configurational changes up through the kilocycle range, but nearest neighbor interactions took over in the megacycle region, leading to moduli of  $10^9$  dynes/cm<sup>2</sup> even for syrupy fluids.*

*In dilute solution, polyisobutylene, polystyrene, natural rubber and polybutadiene microgel exhibited characteristic dynamic viscosities and rigidities depending linearly on concentration. Presumably, this reflects mechanical properties of isolated chains. Some possible models were suggested for the frequency dependence of such properties.*

## INTRODUCTION

The "equilibrium" mechanics of polymers, the giant molecules of plastics and rubbers, have been quite elegantly developed in the range of high strains ("kinetic theory" of elasticity—Meyer,<sup>1</sup> *et al.*). However, the molecular displacements at these strains, and, indeed, much smaller ones, occur, are little understood.<sup>2</sup> Nevertheless, it is essential to know about detailed motions in connecting chemical structure with physical properties. Only in this way can there be obtained from the chemical industry compositions which will serve properly in telephone apparatus.

Other studies have treated one way of getting at these mechanisms by relating stress relaxation, creep, viscosity, etc. to a distribution of molecular relaxation times (and energy barriers), as originated by Kuhn.<sup>3,4</sup> Another approach is to strain polymers with periodic waves over a very wide spectrum of wavelengths, eventually going to frequencies comparable with those of the thermal vibrations of significant groups or segments in the macromolecules. The resulting dispersion or resonance phenomena can then be examined. Hence a mechanical radiation field can interact with the masses of elementary structural units, as the usual electromagnetic field interacts with atomic and group charges. In general, direct interpretations of this kind must be done with shear waves, and, at least, not *only* with longitudinal or ultrasonic waves.

This kind of study is now proceeding using waves generated and followed by piezoelectric crystals connected in as actual electromechanical circuit elements (A. M. Nicolson, 1919). Recent schemes of Mason and co-workers cover the frequency range from  $10 \times 10^3$  to  $60 \times 10^6$  cps, as reported in the paper by Mason and McSkimin in the last issue, while a tuning fork method used by I. L. Hopkins has been applied to "soft" polymers (rubbers) over the range  $10^2$  to  $10^4$  cps (the general range of J. D. Ferry's work at Wisconsin on concentrated polymer solutions).

The relation of these studies to the scientific and technical exploitation of plastics and rubbers is in knowing what a particular chemical composition does to strength, stiffness, ease of molding, impact toughness, etc. That is, are there qualities of the interaction of saturated aliphatic groups that make polyethylene or polyisobutylene have some glass-like as well as liquid-like, or rubbery, nature even at room temperature? If so, conditions causing brittle failures must be watched for. How is the storage of molecular strains in injection molded plastics reduced by increasing molding temperature (when the kinetic theory stiffness per chain actually increases)? These and many similar problems may be generalized under the headings below; in each case the chemical structure of the macromolecule appears to be reflected in relaxation times which combine in different ways to give flow or rigidity, toughness or brittleness.

### *Extrusion and Molding*

Non-Newtonian flow leading to "frozen-in" stresses, subsequent distortion and irregular shapes of plastics<sup>5</sup> and rubbers,<sup>6</sup> implies energy

storage in the sheared molecules. The dynamic shear studies will confirm this. Also dispersion of carbon black and other pigments is restrained by elastic qualities of "liquid" polymers (i.e., instead of "mixing", compounds just microscopically deform and later re-form.) Likewise, the efficiency of compounding<sup>7</sup> and extrusion<sup>8</sup> depend on how quickly the molecules relax after straining.

### *Impact Strength, Brittleness and Tenacity*

Toughness, mechanical shock resistance, ultimate elongation and strength reflect the facility with which the polymer molecules can be displaced without breaking the piece. Thus, they accommodate to the stress by motions presumably similar to those described above. (The situation is complicated when crystallites are also displaced.<sup>9</sup>) In any case, time sensitivity in the range  $10^{-5}$  sec upward exists.<sup>10, 11</sup> The discussion by Morey<sup>11</sup> is a valuable survey of these ideas, and explicitly notes the significance of multiple relaxation processes on damping of shock waves. Evidence of the relation of simple changes in chemical structure to the principle relaxation times effective in these physical properties of plastics and rubbers is thus another part of the dynamics studies. The "brittle point", or volume-temperature transition of amorphous polymers,<sup>12, 13</sup> apparently reflects directly the correspondence of the time of experiment with dominant relaxation time of the polymer.<sup>14, 15</sup> A few measurements on plasticized polymethyl methacrylate (from which, however, no actual rigidities were calculated) indeed indicate abrupt stiffening as a function of frequency at a given temperature.<sup>16</sup> However, the changes measured were too small and indefinite to indicate any particular molecular relaxation. Other work<sup>17</sup> with plasticized polymers is nevertheless concordant with the current findings that molecular relaxations and not long range order determine embrittlement. The converse of this is, of course, that as some "transition" is approached, hysteresis, heat build up, flex cracking and fatigue are greatest.

### *Creep, Stress Relaxation and Recovery*

Even these "long time" qualities of plastics, such as found in cold flow, apparently result from integrated displacements of rapidly oscillating segments of the chains. A most interesting analysis of stress relaxation in rubbers employs Kuhn's suggestion of a particular distribution of relaxation times.<sup>18</sup> The present point is that, again, these relaxation times reflect processes which should appear directly in reaction of the polymer with high frequency shear waves.

From these aspects above the current results of dynamics studies will be reviewed.

#### POLYMER SOLIDS: OVER-ALL MECHANICS

Solid polymers will denote rubbers and plastics in the state in which they are technically used. This is usually their most complex form, with inter- and intra-molecular factors undistinguished. Thus, separation and identification of the main relaxation processes are difficult or impossible. However, it is interesting to consider typical values of modulus and viscosity as related to chemical structure, in the range of frequencies corresponding to extrusion rates, and stresses in actual use.

These values of dynamic modulus and viscosity are distinct from the usual quantities in the literature. The usual expressions are for longitudinal (sound) waves, and give dynamic Young's modulus<sup>19</sup>

$$E^* = E_1 - iE_2$$

$E_2$  measures the out of phase part of the force-displacement relation, and  $E_2 = \omega \cdot$  ("effective viscosity coefficient"). Now, the general elastic constants are  $\lambda + 2\mu$ , with  $\lambda$  = Lamé's constant and  $\mu$  = shear modulus. Here,

$$\lambda + 2\mu = K + \frac{4}{3}\mu,$$

with  $K$  = bulk modulus. Alternately,

$$E_1 = \frac{3K}{\lambda + \mu} \mu = \frac{3\lambda + 2\mu}{\lambda + \mu} \mu.$$

However, in general the present results lead to the simpler shear modulus  $\mu$ . Further the energy losses studied are expressible directly as the usual shear viscosity

$$\mu' = \eta.$$

Previous comprehensive studies of the dynamics of rubbers over significant frequency ranges have yielded loss factors either written as  $E_2/E_1$  (see above),<sup>19</sup> or as a function of the shear viscosity based on Stoke's assumption that the compressional (dilatational) viscosity is zero.<sup>20</sup> But as Nolle<sup>19</sup> and Ivey, Mrowca and Guth<sup>20</sup> clearly recognize, recent work has strongly manifested the presence of compressional viscosity in simple liquids<sup>21</sup> as well as polymeric ones.<sup>22, 23</sup> Hence, the present understanding relating molecular structure to viscosity, plasticity and visco-elasticity is unsuitable for interpreting mechanical wave motion more complex than in shear, unless shear constants are also known.

This sums up to mean that the *chemical* interpretation of basic polymer mechanics requires shear wave measurements. Nevertheless, fascinating evidence of the existence of fine-structure relaxations in polymer solid has come from longitudinal wave investigations.<sup>19, 20, 24, 25, 26</sup> Also, the pioneering shear wave studies of Ferry and collaborators<sup>27, 28</sup> on concentrated solutions of polymers have suggested intrinsic relaxations of the chain molecules in a highly plasticized "semi-solid" state.

The more simplified findings cited below will be seen to unify approaches in this field. Comment must first be made, however, on formulation of experimental results in dynamics of polymers.

### *Expression of Dynamic Properties*

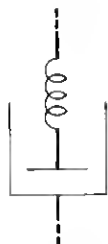
Alternate and equivalent expressions have been thoroughly surveyed;<sup>29</sup> all represent combinations of either Maxwell (series) springs and pistons (elasticity and viscosity) or Voigt (parallel) springs and pistons. Obviously, there is no physical separation of elastic and viscous elements in a polymer molecule, so the irrelevance of the *detail* of the model need not be emphasized. However, the models lead to convenient formulation of *relaxation times* which dielectric studies, in particular, have shown have clear connections with chemical structure. In this chapter, sometimes one and sometimes the other model, or combination, will be used, with the symbols shown on the next page.

Other symbols are sometimes used,<sup>30</sup> but should be easily identified in terms of the above.

### *Rubbers and Soft Plastics*

In Table I, the shear moduli of rigidity,  $\mu$ , and of viscosity,  $\mu'$ , are shown as calculated for the Kelvin-Voigt model, for polymers having the indicated units of structure. The frequencies are from a few hundred to a few thousand cycles, hence, in the range of much technical use, (flexing of tires  $\sim 300$  cps) and rates of shear during processing.<sup>31, 32</sup> Data are from a general study by I. L. Hopkins<sup>33</sup> of the Bell Laboratories, based on a tuning fork transducer introduced by Rorden and Grieco.<sup>34</sup> The strains employed were always small, in the range 0.3 to 1.5 per cent;  $\mu$  and  $\mu'$  were essentially independent of strain, except for some loaded rubber stocks. The  $\mu$  values clearly trace the magnitudes to be expected in going from the most typical rubber (hevea) to the semi-rigid plastics (vinyl chloride-acetate copolymer and plasticized cellulose nitrate). As anticipated from steady-stress observations the "plastics" have  $\mu > 10^7$  dynes/cm<sup>2</sup>. Increase of  $\mu$  with frequency is also greater as

the "plastics" range is approached; a relaxation region is implied. Figs. 1 to 4 show the dispersion of rigidity with frequency in more detail. Especially striking in Figs. 1 and 2 is the small temperature dependence (at least between 27° and 66°C) of  $\mu$ . Because of experimental uncertainty,  $\mu$  cannot be said to be actually higher at the higher temperatures in accord with straight kinetic theory, but at least it is strongly tending that way, as also noted for lower frequencies studies on natural rubber.<sup>19</sup> Nothing like this appears for the plastics; in plasticized nitrocellulose the 100-cycle rigidity decreases 10-fold from 27° to 66°C. This is, then, the second general dynamic quality which reflects the low van der Waals' (dipole, dispersion and induction) forces in hevea rubber and polydimethyl siloxane, as well as their intrachain flexibility. Interchain forces in polyisobutylene (Butyl rubber) are low too, but barriers to flexibility because of sterically hindered-CH<sub>3</sub> groups come in. Table I and Fig. 3

MAXWELL

$\sigma$  = strain  
 $S$  = stress  
 $t$  = time  
 $\tau$  = relaxation time  
 $\tau'$  = retardation time  
 $\mu$  =  $G$  = modulus  
 $\mu'$  =  $\eta$  = viscosity

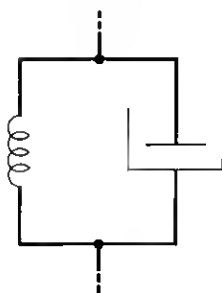
$$\frac{d\sigma}{dt} = \frac{1}{\mu} \frac{dS}{dt} + \frac{S}{\eta}$$

$$S = S_0 e^{-\frac{\mu t}{\eta}} = S_0 e^{-\frac{t}{\tau}}$$

$$\tau = \frac{\eta}{\mu}$$

For const.  $S$ ,  $\frac{d\sigma}{dt} = \frac{S}{\eta}$  or  $\eta = \frac{S}{\frac{d\sigma}{dt}}$

There is same stress on each element; the total strain = sum of single strains.

KELVIN-VOIGT

$$\frac{d\sigma}{dt} = \frac{S}{\eta} - \frac{\mu}{\eta} \sigma$$

$$\sigma = \frac{S}{\mu} \left( 1 - e^{-\frac{\mu t}{\eta}} \right) = \sigma_0 e^{-\frac{t}{\tau'}}$$

$$\tau' = \frac{\eta}{\mu}$$

There is same strain in each element; the total stress = sum of single stresses.

TABLE I

Polymer Unit	Shear Modulus, $\mu$ , dynes/cm <sup>2</sup> 27°C		Shear Viscosity Poises, $\mu'$ , 27°C	
	100 cycles	5000 cycles	100 cycles	5000 cycles
Hevea rubber	$3 \times 10^6$	$5.5 \times 10^6$	350	40
$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \end{array}$				
Polydimethyl siloxane	$0.7 \times 10^6$	$1 \times 10^6$	300	30
$\begin{array}{c} \text{CH}_3 \\   \\ -\text{O}-\text{Si}- \\   \\ \text{CH}_3 \end{array}$				
Polyisobutylene	$5 \times 10^6$	$30 \times 10^6$	8,000	1,500
$\begin{array}{c} \text{CH}_3 \\   \\ -\text{CH}_2-\text{C}- \\   \\ \text{CH}_3 \end{array}$				
Polyvinyl chloride ( $\sim 92\%$ )-acetate ( $\sim 8\%$ ) plasticized by $\sim 36\%$ di- octylphthalate	$13 \times 10^6$	$80 \times 10^6$	25,000	2,000
$\begin{array}{c} -\text{CH}_2-\text{CH}- \\   \\ \text{Cl} \end{array} \quad \text{and} \quad \begin{array}{c} -\text{CH}_2-\text{CH}- \\   \\ \text{O}-\text{C}(=\text{O})-\text{CH}_3 \end{array}$				
Cellulose nitrate	$60 \times 10^6$	$250 \times 10^6$	80,000	4,500
$\begin{array}{c} \text{CH}_2\text{ONO}_2 \\ / \quad \backslash \\ \text{CH}-\text{O} \quad \text{O}-\text{CH} \\ / \quad \backslash \quad / \quad \backslash \\ -\text{C} \quad \text{CH}-\text{CH} \quad \text{CH}-\text{O}- \\   \quad   \quad   \quad   \\ \text{ONO}_2 \quad \text{ONO}_2 \end{array}$				
and $\sim 25$ wt. % Camphor plasti- cizer.				

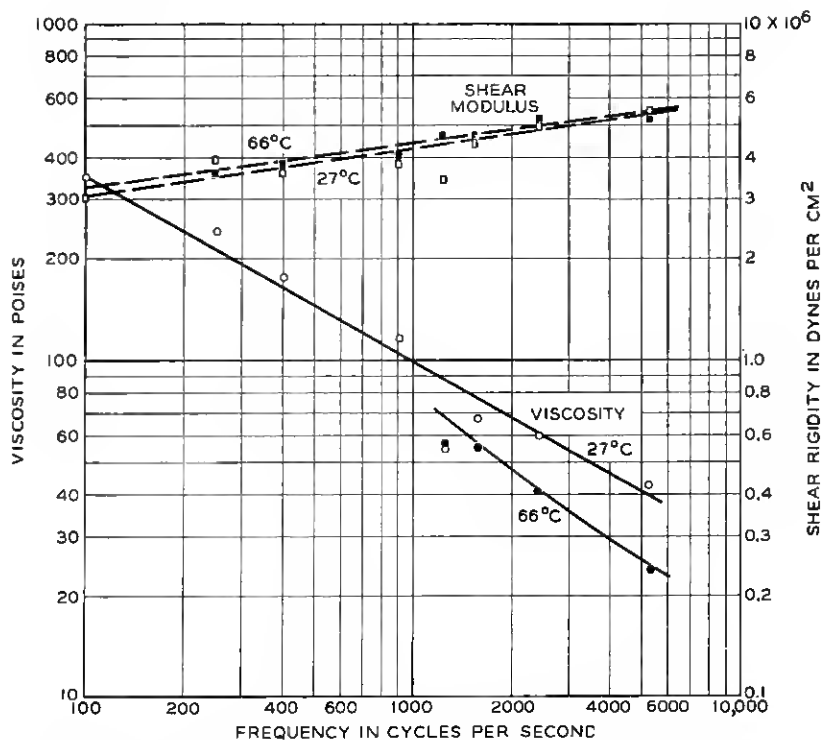


Fig. 1—Viscosity and shear modulus of hevea rubber (cross-linked).

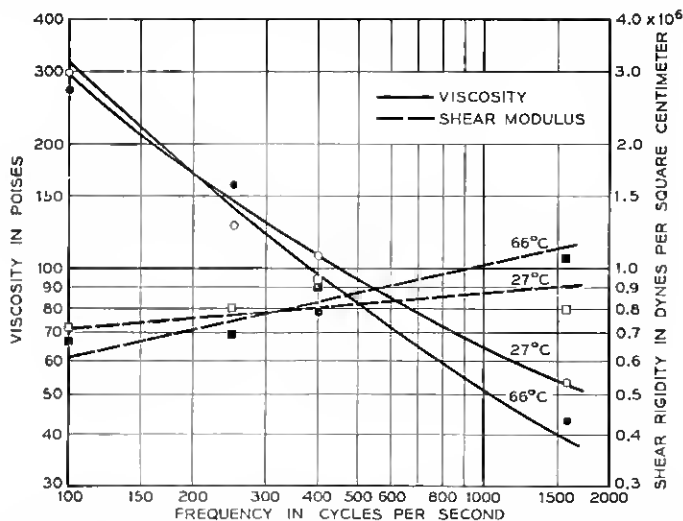


Fig. 2—Viscosity and shear modulus of polydimethyl siloxane (cross-linked).



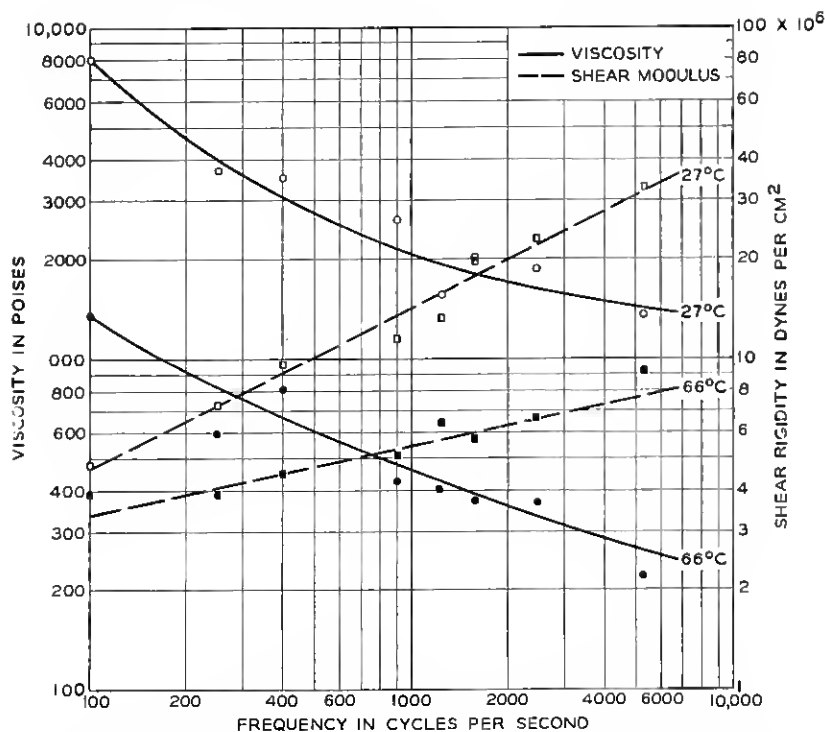


Fig. 3—Viscosity and shear modulus of polyisobutylene (cross-linked Butyl).

emphasize that thinking about the mechanics of a particular chemical structure must include the spatial relationships of groups within the chains, as well as between them.

The dynamic viscosities in Table I are also in accord with the sequence of structures. Their frequency dispersion again connotes varying relaxation processes. Natural rubber's low inner friction, for both compressional<sup>35</sup> and shear waves<sup>36</sup> is famous in its low hysteresis heating. (This unique property is geopolitically crucial, because adequate truck and bus tires cannot yet be made of any other rubber.) Indeed, it is striking that at 100 cycles, a piece of gum rubber has a local viscosity of only 350 poises. The silicone rubber gum also has high elastic efficiency, and its temperature coefficient of viscosity is very low (see Fig. 2), like the thermal coefficients for familiar silicone liquids. It is exciting to speculate in Figs. 1 and 2, whether more precise measurements which Hopkins is now undertaking will confirm the apparently *negative* temperature coefficients of viscosity at some frequencies. "Kinetic theory

viscosity" arising from transfer of momentum among thermally agitated chain segments, does not seem to have been considered in the theory of perfect rubbers. As in gases, it would require an increase of viscosity with temperature.

In polyisobutylene, however, the dynamic viscosity leaps upward in both magnitude and temperature dependence. It should be emphasized that this is, again, for a cross-linked (Butyl) gum—an infinite network like the hevea gum, with presumably infinite macroscopic viscosity. The striking thing is that this internal viscosity is not greatly dependent on the network, at the degrees of "cure" used in rubber technology. For instance, recent studies over the frequency range 20–600 cycles, on high molecular weight,  $\bar{M}_\eta = 1.2 \times 10^6$ , linear polyisobutylene,<sup>37</sup> give, at 25°C and 100 cycles,  $\mu' = 4800$  poises, although the steady flow viscosity of this polymer at this temperature is greater than  $3 \times 10^9$  poises.<sup>38</sup> Then, the infinite network ( $\eta_{\text{steady flow}} \rightarrow \infty$ ) Butyl polymer of Fig. 3 has at 27°C and 100 cycles  $\mu' = 8000$  poises. At 1000 cycles agreement appears to be about the same, and is tolerable considering the several

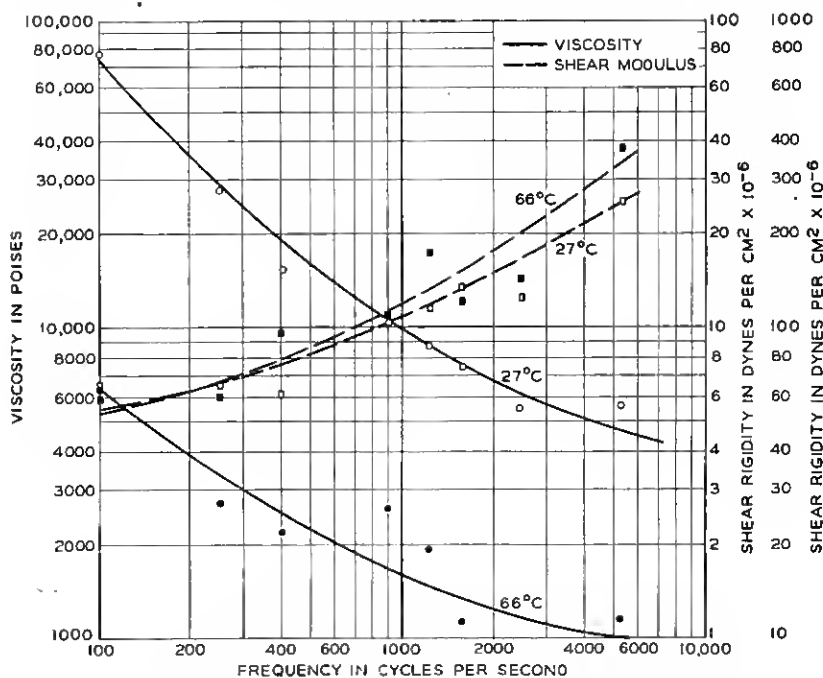


Fig. 4—Viscosity and shear modulus of plasticized cellulose nitrate.

per cent of compounding ingredients in the Butyl gum, and possibility of a small fraction of low molecular weight uncured polymer in it.

Also, wide variations in the degree of cure of Butyl gums were studied without large changes in  $\mu'$ .<sup>33</sup> In this regard, the particular sample of Fig. 3 had an equilibrium swelling ratio (= volume swollen polymer in cyclohexane at 25°C/volume insoluble part of dry vulcanizate) of 4.84. This indicates an  $M_c$  value (average molecular weight between cross-links) of <20,000.<sup>39</sup> Actually many of the dynamic properties can probably be found in individual chain units or segments even smaller than this. This is a significant point in engineering applications where plastics may be cured to reduce creep but where it is desired to retain typical "chain" properties to increase impact toughness. That is, usually some optimum condition for this compromise can be found. The later section on liquids will suggest that physical properties typically associated with chain polymers can indeed reside in even shorter chain sections than the  $M_c$ 's observed in usual gum rubbers.

### Filled Polymers

Marked effects of carbon black and other pigments are of course familiar in both steady and alternating mechanics of rubbers.<sup>19, 24, 35, 36</sup> Brief comment on their influence on dynamic shear properties and thus relaxation mechanisms involved may be directed toward plastics, also, however. Thus, technologically it would be desirable to load thermoplastics with considerable volumes of "inert" fillers, just as is done with rubber. But, almost invariably strength and toughness decline, instead of improving, as in the rubber case. A reason for this appears in investigations by Hopkins when carbon black (a standard type of reinforcing black) was added to Butyl rubber of the sort described in Table I. It is that stiffness seems to rise more rapidly than internal viscosity—i.e., a given strain results in proportionately higher stress than the accompanying internal viscosity provides means for dissipating the stress (as on impact). Hence, the brittleness which fillers normally engender in thermoplastics may represent this change in  $\mu$  vs.  $\mu'$  balance. Table II illus-

TABLE II

Wt. Per Cent of Carbon Black in Butyl Stock	Shear Modulus, $\mu$ , dynes/cm <sup>2</sup> at 27°C		Shear Viscosity, $\mu'$ , Poises, at 27°C	
	100 cycles	5000 cycles	100 cycles	5000 cycles
15.2	$8 \times 10^6$	$60 \times 10^6$	11,000	2,000
28.6	$45 \times 10^6$	$150 \times 10^6$	35,000	3,000

trates some values for Butyl compounds. The swelling ratio ( $SR$ ) for the compound containing 28.6 wt. per cent filler has dropped to 3.2, implying also considerable reductions in  $M_c$  (since theoretically  $(1/SR)^{5/3} = \frac{a}{M_c} - 2bM_c^{39}$ ). Thus, the apparent chain segment between cross-links is shorter than in the unfilled stock (the two were cured to give closely similar degrees of primary valence cross-linkage) and correspondingly the steady-pull modulus is higher. Yet, the internal friction, while also higher, seems to reflect new relaxations from interaction with the filler, and total shock-absorbing power has declined.

### *Microcrystalline Polymers*

The preceding studies at comparatively low frequencies indicated (1) magnitudes of shear rigidity and internal viscosity characterizing rubbers and soft plastics. By familiar shifts of temperature or frequency, they would also apply to polymers known as hard, amorphous plastics at room temperature such as polystyrene and polymethyl methacrylate. (2) Dispersion of  $\mu$  and  $\mu'$  with frequency affirm that the intrinsic or fine structure relaxations have times  $<10^{-3}$  to  $10^{-4}$  sec, and so refer to chemical units much smaller than the average molecules in the usual technical rubbers and plastics. A way to get at what sizes and habits these units might have will be by investigation of low molecular weight polymer liquids. But, while still in the section on solids, it is recalled that microcrystalline polymers such as polyethylene, polyesters (Terylene), polyamides (nylons), cellulose esters, polyvinylidene chloride, polyacrylonitrile etc., have mechanical properties dominated by their crystalline-amorphous ratios.<sup>9, 26, 40, 41</sup> The amorphous volumes are clearly those which donate the flexibility, toughness and shock-resistance of these plastics and textile fibers.<sup>9, 40</sup> An interesting point is, how "viscous" are the disordered chain segments? In an over-all sense, all kinds of dissipation including crystallite friction, analogous to grain friction in metals, scattering of longitudinal waves, and stiffening by low temperatures can occur in these polyphase systems. Thus, effects of chain orientation as well as lateral order (crystallinity) have been detected in dynamics studies.<sup>26, 41</sup> The intrinsically liquid-like or amorphous components of this behaviour—and the things which will correlate most simply with dipole concentration and other chemical features—are most accessible to study at very high frequencies. For, in these polymer solids, unlike the essentially continuous and homogeneous amorphous ones first discussed, the mechanics reflect small regions having widely divergent properties. Thus, methods developed by H. J. McSkimin of Bell Tele-

phone Laboratories (described in the last issue), have been used to probe for elemental reactions at the upper end of the frequencies presently available. Both longitudinal and shear waves were used. In polyethylene, a wavelength for the shear waves was 0.0074 cm., at  $f = 8.55 \times 10^6$  cycles, and in polyhexamethylene adipamide (the usual 6-6 textile nylon), the shear wavelength was 0.0125 cm., for  $f = 8.67 \times 10^6$  cycles, all at 25°C.

The important consequence of these experiments so far has been that, despite the small strains involved, the viscosity appears to be a "polymer" viscosity, rather than an inner friction involving just a few liquid-like atoms per unit. Thus, polyethylene of "equilibrium" crystallinity and average molecular weight corresponding to an intrinsic viscosity in xylene of  $[\eta] = 0.89$  (at 85°C), was measured over the range from 0 to 50°C. The results from both longitudinal and shear wave measurements

TABLE III

Temp., °C.	$f$ , cycles/sec	Viscosity Poises		
		$\mu'$	$\lambda' + 2\mu'$	$\lambda'$
0	$8 \times 10^6$	15	38	8
0	$25 \times 10^6$	5	14	4
30	$8 \times 10^6$	15	34	4
30	$25 \times 10^6$	5	13	3

are given in Table III. These viscosities are expressed in this case for a Kelvin-Voigt model, of rigidity and viscosity *in parallel*. The rigidities associated with these viscosities are about  $3 \times 10^9$  dynes/cm<sup>2</sup>, or not far from the value under steady pull of about  $1 \times 10^9$ .

Now this suggests that the rigid plastic polyethylene retains, even under mechanical impulse of microsecond duration, a shock-absorbing capacity reflected in a shear viscosity of 5-15 poises, and a compressional viscosity of 3-8 poises. The former,  $\mu'$ , may roughly correspond to the liquid viscosity of a paraffin-like chain of from 50 to 65 c-atoms in length. Thus, the dynamics measurements seem to relate to basic premises of polymer structure. These are that the amorphous regions (whose existence is shown quite independently by x-ray scattering, density, heat-capacity, etc.) indeed take up and dissipate sudden stresses which the microcrystallites, despite their great strength, would be too brittle to sustain.

These results give hope that further probing of the dynamics of liquid-like elements in rigid plastics will eventually lead to precise adjustment

of molecular weight, chemical structure (degree of branching in polyethylene), crystallinity, etc. These quantities, when fitted to a given pattern of  $\mu$ ,  $\lambda$ ,  $\mu'$  and  $\lambda'$  at proper frequencies would yield plastics of optimum serviceability under the multitude of stresses encountered in use.

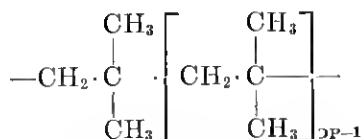
A similar liquid-like structure—even where the (crystalline) rigidity is much higher<sup>40</sup> and mobile chain segments smaller—apparently occurs in polyamides. Presumably the hydrogen bonding and dipole interactions are very imperfect in the disordered regions,<sup>40</sup> and there the chain interaction is reminiscent of polyethylene. For instance, in polyhexamethylene adipamide, measurements in the 8 to 30 megacycle range do indicate that the Lamé elastic constant  $\lambda$  is about  $5.6 \times 10^{10}$  dynes/cm<sup>2</sup>, but only about  $3 \times 10^{10}$  for polyethylene. This reflects over-all stiffness dominated by crystallites. Nevertheless, the compressional viscosity,  $\lambda'$  is 17–6 poises (going from 8 to 30 mc) for the polyamide, but only 5–2 poises for polyethylene. Of course, since there is dispersion in both cases, these relative magnitudes might be quite different at some other frequency or temperature (all above are at 25°C). Yet it remains that the nylon, despite its hardness, also has a liquid-like component more viscous than that of polyethylene. Similar relations appear in the shear viscosities,  $\mu'$ , also determined for these two systems. For the 6–6 polyamide,  $\mu'$  goes from 19 to 7 poises over the 8 to 30 mc interval while polyethylene changes from 15 to 5. These quantities indicate again, as with the polyethylene, that “polymer liquids” rather than just a few small groups of atoms are the important mechanical elements even at frequencies of  $10^7$ . Now polystyrene, an amorphous polymer, also has rigidities of about  $10^{10}$  dynes/cm<sup>2</sup> but the  $\mu'$  and  $\lambda'$  values at room temperature are far below 5 to 20 poises, and glass-like brittleness (although not so bad as silica glass) results.

So far, then, the two characteristic extremes of polymer mechanics have been discussed: (1) the soft rubbers, whose dynamics at low kilocycle frequencies imply, at ordinary temperatures, predominantly overlapping combinations of relaxation processes whose relaxation elements involve many segments per molecular chain; and (2) the hard, microcrystalline plastics, whose behaviour is predominated by relaxation processes having times of  $10^{-6}$  to  $10^{-7}$  sec because the longer period (slower) displacements have been relaxed out at the temperatures of normal use. (Likewise, interconvertibility by temperature<sup>19</sup> between these two extremes is presumed. Also, a certain correspondence between dielectric and dynamic relaxations in these classes is indicated.<sup>41a</sup>) Next, it is in-

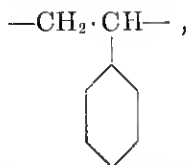
teresting to see what are the simplest structures (particularly in terms of molecular weight) yielding these effects. In other words, what kind of liquid really exhibits "polymer mechanics?" No detailed answer to this can be given below, but results on some polymer liquids of low average molecular weight will indicate that the mechanisms in rubbers and plastics are probably more general than previously supposed.

#### POLYMER LIQUID MECHANICS

By techniques described in detail elsewhere,<sup>22,23</sup> a series of polyisobutylene liquids have been investigated. These polymers were made by ionic catalyzed mass polymerization at reduced, but not very low, temperatures. While no great care to purify the monomer was used, such polymerizations require fair purity to go at all. Seemingly, the resulting liquids do represent a polymer homologous series, although head-to-tail sequence of the monomer units, some single ethyl rather than paired methyl side groups, etc., may differ slightly from the higher molecular weight forms in Butyl rubber and polyisobutylene gum. Whatever are these details, it appears that the polymers represent a linear hydrocarbon chain, with essentially two methyl groups on every other chain atom:

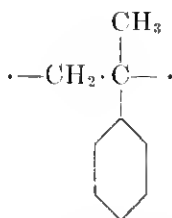


By contrast, polyethylene, with the nominal chain  $\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---CH}_2\text{---}$  and to a lesser extent polystyrene,



have chains in which rotation about the bonds is less sterically hindered. The final section, on isolated polymer chains (in dilute solution), will consider this aspect further. However, some results will be reported below on a low molecular weight poly- $\alpha$ -methyl styrene, which may be considered structurally a cross between the rubber, polyisobutylene, and

the plastic, polystyrene,



Other studies in progress on liquid polybutadiene, polyisoprene, polypropylene, and polypropylene sebacate from which further information about intra-chain stiffness may be derived, will also be noted.

Properties of the polyisobutylenes studied are summarized in Table IV, some additional molecular weights in this range appear as extra points in some of the high-frequency graphs. The molecular weights  $\bar{M}_\eta$  are "intrinsic viscosity" averages<sup>42, 42a</sup> and, with reasonable estimations of the  $\frac{\bar{M}_\eta}{\bar{M}_n}$  ratio, check with cryoscopic number average,  $\bar{M}_n$ , values on such materials, which are in turn listed in the table as expressed by melt viscosity relations of Fox and Flory.<sup>42a</sup> These molecular weights repre-

TABLE IV

Polyisobutylene Polymer	$\overline{DP}_\eta$	$\bar{M}_\eta$	$\bar{M}_n$	25°C viscosity Poises	Maxwell $\mu$	Voigt $\frac{\mu'}{\mu}$ Poises	Maxwell $\frac{\mu'}{\mu}$ Poises	Freq. Cycles
A	10	565	318	0.37	$3 \times 10^8$	0.6	0.6	$14 \times 10^6$
A"	30	1660	697	39.6	$6.2 \times 10^6$	16.5	18.8	$2 \times 10^4$
					$1.7 \times 10^9$	7.9	10.0	$14 \times 10^6$
B	45	2520	1070	216	$3 \times 10^9$	15.2	24.2	$14 \times 10^6$
C	56	3350	1720	737	$3.6 \times 10^9$	20.2	47.9	$14 \times 10^6$
D	74	4170	2530	1840	$4.5 \times 10^9$	23.4	78.9	$14 \times 10^6$
E	147	8240	4850	4600	$5.3 \times 10^9$	27.2	92.3	$14 \times 10^6$

sent reasonable averages rather than absolute values for these heterogeneous polymers. The  $\overline{DP}$  values are just the number of isobutylene units per average chain. The  $\eta$  values are the steady flow viscosities at low rates of shear—usually determined by a falling ball.

#### *Rigidity and Viscosity Magnitudes*

The properties of these liquids ranging from polymer A having only forty times the viscosity of water to E, which begins to approach fluidities of technical polymer melts (polyamides, for instance), were explored



in the kilocycle range with shear waves generated by torsional crystals and in the megacycle region by shear waves with the reflectance method and by longitudinal (ultrasonic) waves from a pulse propagation technique.<sup>23</sup> The results have been expressed in two ways. First, in earlier reports,<sup>22, 23</sup> a trend corresponding with experiment was given by two Maxwell elements arranged in parallel. This result is too simple compared to the distributions of relaxation times previously proposed for high molecular weight polymers to reproduce *detailed* observation. Nevertheless, perhaps because of the smaller molecules involved, there seems to be clear indication that two *principal* relaxations predominate the mechanical reactions of these liquids over the range of frequencies of present interest,  $10^2$  to  $10^7$  cps. For example, for polymer D, these are:

First Relaxation	Second Relaxation
$f_c \sim 4 \times 10^3$ cycles $\mu \sim 4 \times 10^7$ dynes/cm <sup>2</sup>	$f_c \sim 5 \times 10^6$ cycles $\mu \sim 6 \times 10^9$ dynes/cm <sup>2</sup>

(In accounting for the second main relaxation, a hysteresis component had to be introduced whose significance has been suggested.<sup>22</sup>)

Second, specific values of shear rigidity  $\mu$  (Maxwell) and  $\mu$  (Voigt), shear viscosity  $\mu'$  (Maxwell) and  $\mu'$  (Voigt) as well as the constants for related compressional wave systems,  $\lambda + 2\mu$  (elastic) and  $\lambda' + 2\mu'$  (viscous) have been calculated for particular frequencies. Unlike in the first way of expression, these latter quantities are all highly frequency dependent. However, they describe conditions at various frequencies of interest, and are thus often worthwhile.

Both ways of looking at the data lead, as implied by the figures above, to the proposal that typical polymer *stiffness* (shear rigidity of  $\sim 10^7$  dynes/cm<sup>2</sup>) is present at  $\bar{M}_\eta \sim 1600$ , with  $\bar{DP}_\eta \sim 30$ , or an average chain length of about 60 carbon atoms. This appears when the straining is done in  $10^{-3}$  to  $10^{-4}$  sec. In the  $10^{-6}$  to  $10^{-8}$  sec range, rigidity occurs for even an average chain length of 20 atoms as shown in Table IV.

#### STRUCTURAL FACTOR IN LIQUID MECHANICS

The main relaxations in the kilocycle range in polyisobutylene liquids seem to lead to quasi-configurational elasticity. This is where the kinetic theory tendency for a most probable separation of chain ends is retarded by viscous interaction of segments between and within the chains. Hence, the middle dashed curves of Fig. 5, showing shear elasticity for some of the polymers of Table IV, decrease exponentially with increasing tem-

perature. While pure kinetic theory elasticity would give a modulus *increasing* linearly with increasing temperature, these systems, like all practical rubbers and plastics, actually grow softer with rising temperature when deformed dynamically. It is striking, nevertheless, that a modulus of  $\sim 10^7$  dynes/cm<sup>2</sup> seems characteristic of the visco-elastic energy storing of these simple polymer structures. As noted below this is  $10^3$  less than the crystal-like, close-packed, stiffness found for these same molecular frequencies above their second principal relaxation time.

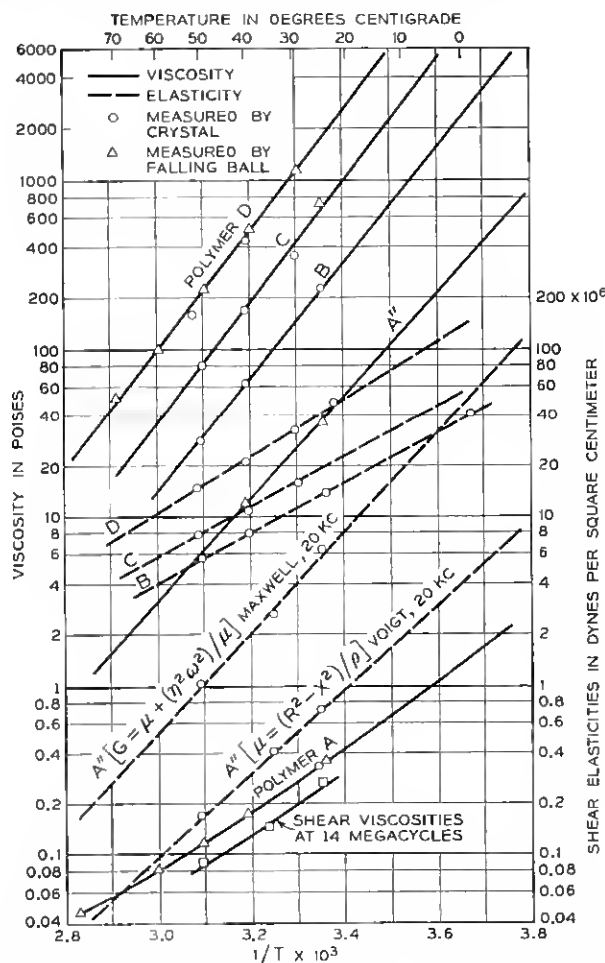


Fig. 5—Shear elasticities and viscosities of polyisobutylene liquids assuming a Maxwell model with relaxation frequencies  $10^3$ – $10^4$ . (Lower dashed curves for frequency-dependent models.)

Thus, it seems that the former,  $10^7$ , modulus is typical of the structural arrangements in polymers said to be above their second order transition temperatures<sup>12, 13</sup> while the second,  $10^9$ , modulus reflects interactions below the freezing-in.

These conclusions obtain regardless of the particular expression of the data. But, for comparison, curves are shown on Fig. 5 for a polyisobutylene A'' in which the dynamic modulus  $\mu$  at 20 kc is computed for both Maxwell and Voigt elements. The two points denoting the steady flow viscosity of polymer A'' rank it with respect to the others in the series.

Apparently even very fluid polymer melts, chain molecule plasticizers, and small segments of long molecules must be expected to show appreciable rigidity when stressed rapidly. Referring to the introduction it is reasonable that rough extrusions, frozen-in molding stresses and the like are so easily produced. The lines of Fig. 5 are not, of course, implied to be linear over any considerable temperature range. In the region represented, the temperature coefficient for viscous flow is about 16 kcal for the B, C and D liquids (about 12 for A). This agrees roughly with the steady flow values found for very high molecular weight polyisobutylene.<sup>38, 42a</sup> The temperature coefficient for the rigidity is less, as would be expected, since the whole center of gravity of the chain need not be displaced, but only local segments.

This quasi-configurational elasticity is increased by molecular weight (although kinetic theory elasticity of chain segments in a network is decreased by increasing segment length). The  $\log \mu$  vs density at 25°C plotted in Fig. 6 indicates that the chief influence is the number of chains per cc, since the points for all the molecular weights now lie on a single line. It should be repeated that the elasticity modulus plotted,  $\mu$ , is again for a roughly frequency-independent or "absolute" model.<sup>22, 23</sup> The same is true for the three solid lines on Fig. 6, showing  $\mu$  in the second, or  $10^7$  cycle, relaxation range. Here effects of detailed liquid structure come out; the three average molecular weights no longer lie so nearly on a single line. This elasticity is presumably from the crystal-like interaction of nearest-neighbor segments. If temperature is adjusted so that densities are the same, it is seen that the *lower* average molecular weight liquid has the *higher* elasticity modulus. This difference is not large, and should not be interpreted as showing an equal segment interaction, for a polymer of lower specific volume (B compared to D). Rather, it emphasizes in this relaxation range, approaching the "glass" behaviour, that the relaxation rate is vastly more temperature dependent than the specific volume change alone, and structural variations in the

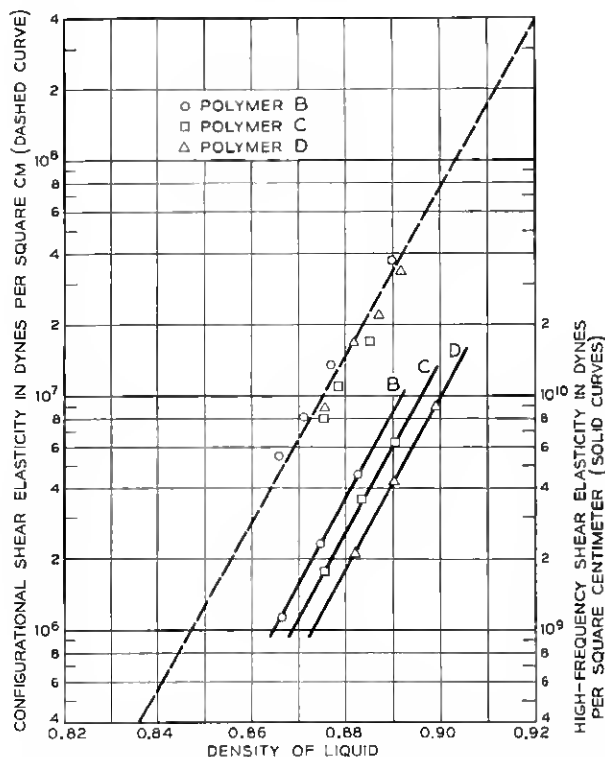


Fig. 6—Principal shear elasticities of polyisobutylenes as related to their densities.

packing of segments in the liquid (coordination number, etc.) become important.

#### *"Soft" and "Hard" Liquid States; Second Order Transitions*

A recent noteworthy study<sup>43</sup> of volume-temperature and viscosity-temperature changes in polystyrene (with a note on polyisobutylene) brings out many points in common with ideas of polymer liquid structure indicated by the dynamics work.<sup>22, 23</sup> Particularly, the fact that according to steady state measurements, the "local configurational arrangement of the polymer segments"<sup>43</sup> below  $T_g$  remains fixed accords with the postulations from dynamics work. That is, above the second main relaxation, it seems to be just the interactions in these fixed arrangements which cause the glassy (or "crystalline") dynamic modulus of  $10^9$  to  $10^{10}$  dynes/cm<sup>2</sup>. Further, the point that  $T_g$  is *not* an isoviscous state for polymers<sup>43</sup> agrees with the dynamics result that macroscopic

viscosity of the polymer has relatively little to do with the actual values of dynamic viscosities. These would be at frequencies where the response of the polymer liquid to the mechanical field is determined only by motions within the local fixed arrangements mentioned above.

Fig. 7 illustrates this, where on one scale the macroscopic viscosity is plotted according to the familiar log-log relation with molecular weight. Two extremes of average molecular weight,  $\bar{M}_n$  and  $\bar{M}_\eta$ , are used for the liquids, to show that the molecular weight distribution does not alter the general conclusions. ( $\bar{M}_\eta$  is an upper limit weight average figure.) On the other scale, the dynamic viscosity  $\mu'$ , in this case for a single element frequency-dependent Voigt model, shows low values and marked curvature. These betoken the relaxation in which molecular weight, through its effect on free volume and other structural factors, is signif-

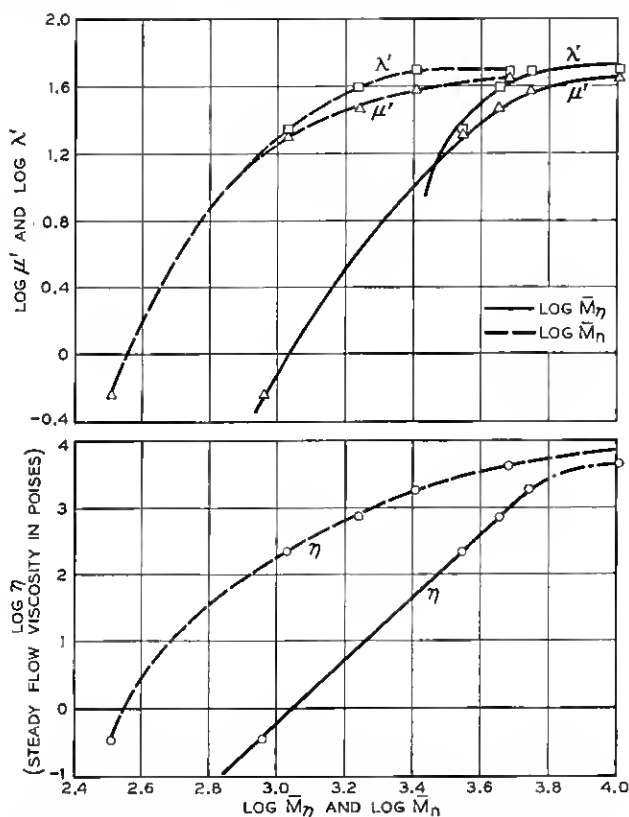


Fig. 7—Comparison of steady flow and dynamic viscosities (at 25°C and 8 me) of polyisobutylene liquids of different molecular weights.

icant for displacements superficially quite different from those in macroscopic viscosity.

The compressional viscosity,  $\lambda'$  is also plotted, for the same model, in Fig. 7. It is, within experimental error, zero for polymer A', as determined by shear and compressional wave studies at 8 mc frequency.<sup>22</sup> This is a rare case, then, where the attenuation of sound waves through a liquid has been quantitatively accounted for by the shear viscosity. But, as soon as the average molecular weight rises to 1000 or so,  $\lambda'$  comes in clearly, and the new mechanism for dissipating compressional or dilatational stresses is developed. As this presumably represents directly free volume or coordination number changes in liquid structure,<sup>44, 45</sup> its detailed study near  $T_g$ ,<sup>43</sup> and in connection with brittle points of rubbers, may eventually be especially fruitful.

Another depiction of influence of average molecular weight in these liquids on dynamic viscosities occurs in Fig. 8. Here, the  $\lambda'_c$  curve is

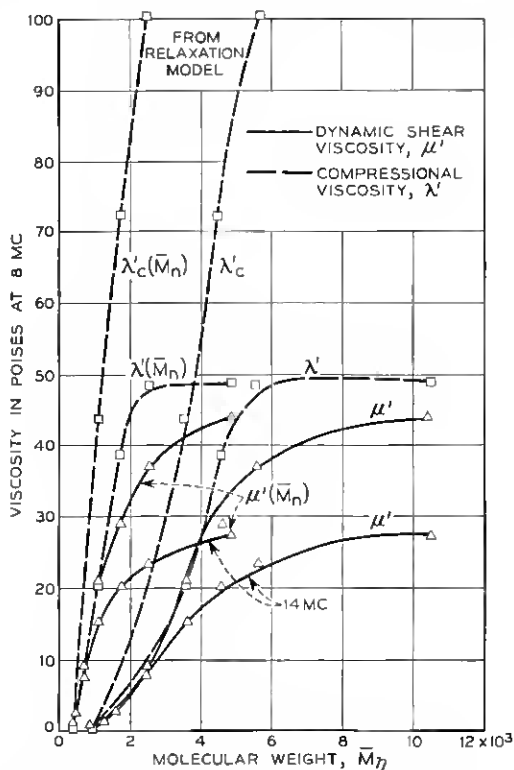


Fig. 8—Dynamic viscosities of polyisobutylene liquids as function of average molecular weight (25°C).

for, again, a crude model attempting to show compressional viscosity over the whole frequency range, while the other viscosities are Voigt expressions at 8 (or 14) mc. Extremes of molecular weight averages are shown.

Comparison of the "soft" or quasi-configurational rigidities, expressed, like the  $\mu$  of Fig. 5 as relatively frequency independent  $\mu_c$ , with the "hard" or glassy rigidities is given in Fig. 9. The  $\lambda$  and  $\mu$  values are for the Voigt model at 8 mc. The graph does not show the bend-over of the "soft",  $\mu_c$ , curve with molecular weight, but that happens more gradually. The "hard" rigidities  $\lambda$  and  $\mu$  quite readily show this inflection. As before, the relaxing segments must be  $< 100$  chain atoms, according to the behaviour of the molecules at room temperature.

Concerning influence of molecular weight on engineering "brittle points" of such importance in rubber technology, the present studies agree with earlier proposals. Thus, although the  $T_g$  or  $v$ - $T$  second order transition point always decreases with decreasing molecular weight,<sup>43</sup>

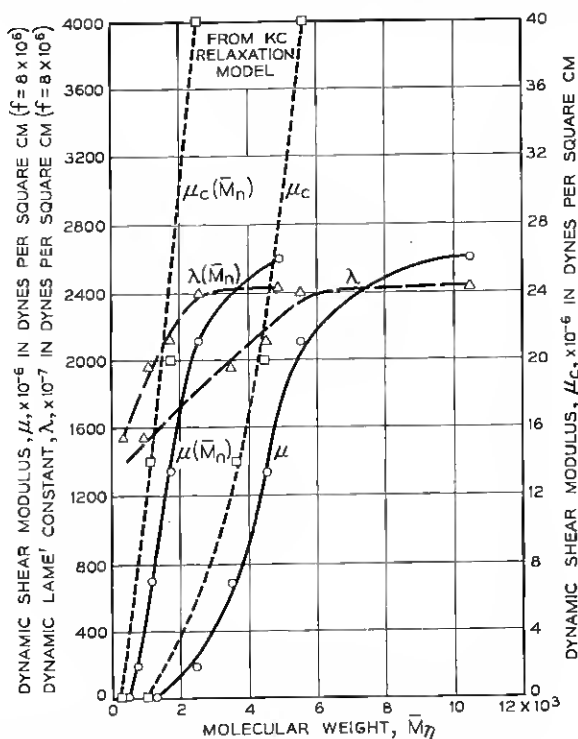


Fig. 9—Dynamic rigidities of polyisobutylene liquids as function of average molecular weight (25°C).

the brittle point tends to increase as the molecules get smaller. This was supposed to be because the ultimate elongation (doubtless due to viscoelastic or quasi-configurational elasticity and not kinetic theory elasticity as sometimes said) declined with chain length, so that the specimen broke at lower and lower strains,<sup>13</sup> even though it was not really in the glassy state. Now, the results above<sup>22, 23</sup> demonstrate that the shear modulus at a given temperature does fall off for average molecular weights of polyisobutylene below  $\sim 5000$ . Hence, the mechanical embrittlement of the low molecular weight samples is not because they are stiffer, but because they are weaker.

#### POLY- $\alpha$ -METHYL STYRENE: A "PLASTIC" LIQUID

Most of the liquid studies have been on polyisobutylene polymers, made "hard" or "soft" by temperature or frequency, but under use

TABLE V

Poly- $\alpha$ -methyl styrene	$\eta$ Poises	$\mu'$ , 14 mc, Poises		$\mu$ , 14 mc dynes/cm <sup>2</sup>	
		Maxwell	Voigt	Maxwell	Voigt
I	242	111.4	23.6	$5.1 \times 10^9$	$4 \times 10^9$
II	4340	502.7	14.3	$7.6 \times 10^9$	$7.4 \times 10^9$

conditions, considered rubbery. If one of the methyls in polyisobutylene is replaced by a phenyl, poly- $\alpha$ -methyl styrene, a hard plastic is produced. Low molecular weight polymers of this composition are, however, liquids at room temperature. Hence, it is interesting to compare their reaction to mechanical waves with that of polyisobutylene liquids of similar macroscopic viscosity. Table V lists a few properties at 25°C.

Polymer I has roughly the steady flow  $\eta$  of polyisobutylene B. Also, the Voigt  $\mu'$  at 14 mc is similar: 15.2 poises compared to the 23.6 poises of the poly- $\alpha$ -methyl styrene. However, the Voigt  $\mu$  is already 50 times higher for the phenyl substituted chain. (This shows the shift of the second relaxation range, of course, where nearest neighbor interactions rule.) Even more striking, the temperature coefficient of a  $\mu'_c$ , calculated as the second principal shear viscosity in a frequency independent model,<sup>23</sup> as before, is about 24 kcal, compared to about 12 for  $\mu'_c$  for polyisobutylene in its similar model. Thus, although there was no apparent difference between the mechanical properties of these two polymer liquids in their room temperature state, their dynamics diverged remarkably. This was when they were studied with shear waves whose



frequencies approached the glass-into-rubber relaxation times. Clearly, again, individual interaction of chain-like chemical units and not any micellar or other special aggregation of them, predominates polymer mechanics.

It still remains, however, to separate interactions of the basic units within and between chains. Most likely, the model plastic vs rubber liquids just discussed differ in the high frequency region substantially *only* because of *inter-chain* forces between phenyl vs methyl groups. However, especially in the high-frequency region, questions of *intra-chain* structure, such as the steric hindrance of adjacent pairs of methyl groups in polyisobutylene, restricted rotations about bonds, etc., come in. Obviously where configurational or quasi-configurational displacements are important, as in all cases of elongation >20 per cent (this is certainly an *upper* limit), flexibility of single chains needs to be understood. This is built deeply into chemical structure; plasticizers presumably may change over-all configuration as well as modify interaction, but they are impotent to vary flexibility. Accordingly, problems of rubber, usable in the Arctic, and of wire and cable insulation bendable at low temperatures always come back to whether the polymer chain bonds have free rotation. Some examples of the combinations of effects within and between chains can indeed be shown in several other polymer liquids which are rubber models.

This influence of small changes in chemical structure is compactly illustrated by comparing a few other hydrocarbon polymer liquids with polyisobutylene. Also, rather dilute dipolar groups have been introduced in the linear polyester liquid polypropylene sebacate, whose structure is otherwise like that of hydrocarbons.<sup>45a</sup> In Table VI, liquids of the given structure with some (unknown) distribution of molecular weights, were studied with shear waves at 77 and 142 kc at a temperature where each had the same steady flow viscosity. The figure chosen was 700 poises, and the temperature range required to adjust to it in the series was 10.9° to 85°C, meaning that the liquids had comparable consistencies at ordinary temperatures.

Despite these similarities under steady stress, the retardation times,  $\tau'$ , vary three-fold, with the highly substituted hydrocarbon chains, polyisobutylene and polypropylene, the highest. Despite the intermolecular action of the dipoles in polypropylene sebacate, the low polymer has a short retardation time, although its "brittle point" with decreasing temperature is far above that of polybutadiene or even polyisobutylene. Presumably the flexibility around C—O—C bonds rather compensates for increased dipole interaction. Where both low polarity

TABLE VI.—*Dynamic Properties of Polymer Liquids of Varying Structure.*

Polymer	°C	Den- sity, g/cc	$\eta$ Poles	Voigt				Maxwell			
				77 kc		142 kc		77 kc		142 kc	
				$\eta$ Poles	$G_1$ dynes/cm <sup>2</sup>	$\eta$ Poles	$G_1$ dynes/cm <sup>2</sup>	$\eta$ Poles	$G_1$ dynes/cm <sup>2</sup>	$\eta$ Poles	$G_1$ dynes/cm <sup>2</sup>
							$\tau' = \frac{\eta}{G}$ sec				$\tau = \frac{\eta}{G}$ sec
							142 kc				142 kc
Polyisobutyl- ene C	25.40	.8857	700	165.1	$3.5 \times 10^7$	134.2	$6.4 \times 10^7$	197	$2.2 \times 10^8$	173	$3 \times 10^8$
Polypropylene	85.0	.8248	700	23.6	$6.5 \times 10^6$	22.0	$9.9 \times 10^6$	$22 \times 10^{-7}$	$31.3 \times 10^7$	27.5	$5 \times 10^7$
Polybutadiene	10.9	.8767	700	7.2	$5.5 \times 10^6$	5.2	$6.3 \times 10^6$	$8 \times 10^{-7}$	$25.1 \times 10^7$	14.5	$1 \times 10^7$
Polypropylene Sebacate	41.7	1.0421	700	12.7	$9 \times 10^6$	8.5	$11.6 \times 10^6$	$7 \times 10^{-7}$	$1.3 \times 10^7$	28.6	$1.7 \times 10^7$
								40			$17 \times 10^{-7}$

and chain flexibility obtain, as in polybutadiene and the silicones, dynamic properties apparently accord with brittle points in implying small temperature coefficients of relaxation times. In fact, the temperature coefficient for dynamic viscosity of polybutadiene is only about 1.5 kcal, whereas a comparable figure for polyisobutylene and polypropylene is 12 kcal.

The frequency range in which the structural comparisons above were made, resides, as discussed earlier, in the zone of configurational viscoelasticity. That is, over-all shape changes, rather than just nearest neighbor interactions, are predominant even at these comparatively short average chain lengths. Now, other recent studies of polyisobutylene liquids, at 5 to 100 cps frequency, exhibit no rigidity at 25°C and above, although they become non-Newtonian rapidly as temperature is

TABLE VII. *Shear Dynamics of Polyisobutylene A''.*

$$(\bar{M}_n = 1660; \eta_{\infty}^{25^\circ} = 39.6 \text{ Poises})$$

T, °C	Freq., cps	Voigt		Maxwell	
		$\mu$ dynes/cm <sup>2</sup>	$\eta$ Poises	$\mu$ dynes/cm <sup>2</sup>	$\eta$ poises
25	266	$3.8 \times 10^3$	39.2	$1.2 \times 10^6$	39.3
25	1601	$4.8 \times 10^4$	38.4	$3.1 \times 10^6$	39.0
27	25300	$5.4 \times 10^5$	19.9	$1.9 \times 10^7$	20.5
27	41390	$1.5 \times 10^6$	19.9	$1.9 \times 10^7$	21.5
27	53060	$1.5 \times 10^6$	18.1	$2.6 \times 10^7$	19.3

reduced.<sup>45b</sup> The questions are, where does the configurational elasticity drop out, as frequency is reduced at 25°C; and does it seem reasonable that this dispersion correlates with a shift in frequencies at lower temperatures. Partial answers are given by very recent studies of I. L. Hopkins of Bell Telephone Laboratories. He has equipped the tuning fork vibrator described earlier<sup>33</sup> with two parallel vanes filled in between with a film of polymer liquid. Pure shear properties can be derived from the response of this system. Table VII lists a few typical figures obtained on polyisobutylene polymer A''. These indeed show that the kilocycle relaxation zone (some new data by McSkimin's torsional pulse method are given for it) extends smoothly down to where dynamic and steady stress viscosities are equal. Seemingly there are no new "extra long time" relaxation mechanisms; probably the slow relaxation times sometimes indicated for high molecular weight rubbers are just displacements of this configurational relaxation to long times because of high molecular weight and internal viscosity.

By contrast to the conclusions associated with the data of Table VII,

some observations at low frequencies on isoviscous properties of polyisobutylenes A" and C indicate nearly *identical* retardation times. Thus A" at 25°C and C at 61°C have  $\eta_s = 39.6$  poises. The  $\eta$  values at 266 and 1600 cps are also about 39 poises,  $\mu$  at 266 cps is 3800 dynes per cm<sup>2</sup> for both liquids, and at 1600 cps is from  $3.5 \times 10^4$  to  $4.8 \times 10^4$  dynes per cm<sup>2</sup>.

In the final section, mechanical waves have been used to explore dilute polymer solutions, to see how isolated molecules behave, free of interaction with each other.

#### DILUTE POLYMER SOLUTIONS

##### *Physical Principles in Measurements*

Precise information on dynamics of solutions approaching infinite dilution (and thus complete separation of the polymer chains) is desired here. Again these must be shear dynamics; bulk rigidity of ordinary liquids is so high that a few polymer molecules added cause little effect. Dilution is emphasized because even at 1 per cent by volume, high polymer molecule coils frequently interact, especially in "good" solvents. Thus, several workers have detected shear rigidity in polymer solutions, in one case for polymethyl methacrylate of average molecular weight 320,000, at 1 per cent concentration in *o*-dichlorobenzene.<sup>46</sup> Very low frequencies used ( $\sim 10$  cycles) there and in an earlier study<sup>47</sup> suggest, however, that even here, appreciable entangling of the molecules created a temporary network such as studied by Ferry.<sup>27, 28</sup> Such was certainly present in the 5 to 18 per cent solutions of cellulose acetate in dioxane measured in one of the earliest observations of shear rigidity in polymer solutions.<sup>48</sup>

Accordingly, since strictly linear, and hence non-interacting, mechanics are sought for the macromolecules in dilute solution, careful evaluation of experiments is essential. Since already it appears that important over-all (quasi-configurational) relaxations occur for, say, polyisobutylene in the kilocycle range, and it is suspected that not *all* of the interactions involved are between chains, the torsional crystal techniques are attractive. The absolute viscosity of these solutions is very low, so the ammonium dihydrogen phosphate crystal whose piezoelectric qualities are appropriate for polymer liquids in the circuits previously noted<sup>22, 23, 49</sup> is advantageously replaced by quartz.

Detailed electromechanical behaviour of such crystals in the pure liquids cyclohexane and benzene is of first concern. The electric field applied to electrodes on the suspended crystal produces mechanical

torsion generating pure shear waves. These waves may be modified by the environment around the crystal (vacuum, gas, liquid, solid) and react back. Thereby a mechanical resistance,  $R_M$ , and a mechanical reactance,  $X_M$ , are imposed on the electrical properties of the crystal element in the circuit. This connection comes out as:

$$\begin{aligned}\Delta R_E &= K_1 R_M \\ \Delta f &= -K_2 X_M,\end{aligned}$$

where  $\Delta R_E$  is the increase in measured electrical resistance of the crystal element in the medium compared to in vacuum (or practically in *dry* air or nitrogen). The decrease in resonant frequency of the crystal element under these conditions is  $\Delta f$ . Thus  $K_1$  and  $K_2$  are electromechanical constants, which fundamentally may be calculated from the dimensions and piezoelectric constants of the crystals.<sup>49</sup> Now, in simple, Newtonian liquids,

$$R_M = X_M = \sqrt{\pi f \eta \rho}$$

Thus, by carefully measuring  $\Delta R_E$  (or  $\Delta f$ ) on a liquid of accurately known density  $\rho$  and viscosity  $\eta$ , at a given frequency  $f$ , and a given temperature, the constants  $K_1$  and  $K_2$  may be evaluated without assumptions and approximations of deriving them. Their constancy will then reflect the electromechanical stability of the system. Their behaviour under various conditions will be illustrated below. One further point is that when a liquid or solution does exhibit shear rigidity, or, in other words, if the single large molecules in a dilute solution are able to store energy, then  $R_M > X_M$ . Hence, in this case, the observed quantities  $\Delta R_E$ , and especially  $\Delta f$  require particular precision.

In this regard, typical magnitudes of change of  $f_R$  between *dry* air and pure cyclohexane, at various temperatures, appear in Fig. 10. Questions often arise as to the arbitrariness of suspension of the radiating crystal, by the fine supporting and lead wires. The effects with the plain wires, in the solid curves of Fig. 10, are somewhat, but not radically, changed when a metal bead is put on, heavily loading vibrations in the wires, as shown by the dashed curves. In Fig. 11, a somewhat larger influence of the loaded support wires is shown for the  $R_E$  values, but both curves, by their smoothness and shape over a temperature range where the thermal expansion and other elastic constants of the metal support wires are quite different from those of the quartz crystal, affirm reliability of mounting and electromechanical coupling.

Fig. 10 shows, even for an 80-kc crystal, that  $\Delta f$  for an organic liquid

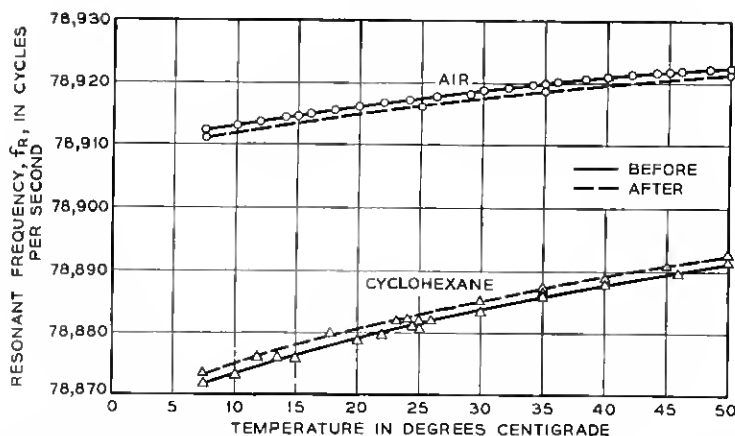


Fig. 10—Temperature variation of resonant frequency before and after adding weights to mounting wires.

(or dilute polymer solution) is bothersomely small. An excellent oscillator at 20 kc can hardly be expected to drift less than  $\pm 2$  cycles, but at 20 kc the  $\Delta f$  like that between the sets of curves on Fig. 10 might be only 10 cycles, so 20 to 35 per cent error could come in. Hence, a different scheme for measurement of  $f_r$  than that in earlier systems<sup>23, 49</sup> was evolved. The tenth harmonic of the (say 80 kc) resonant frequency was beat against the 79th harmonic of a controlled standard 10-kc frequency. An interpolation oscillator accurately readable to 1 cycle then supplies the many hundred (roughly 1000) difference between these two high

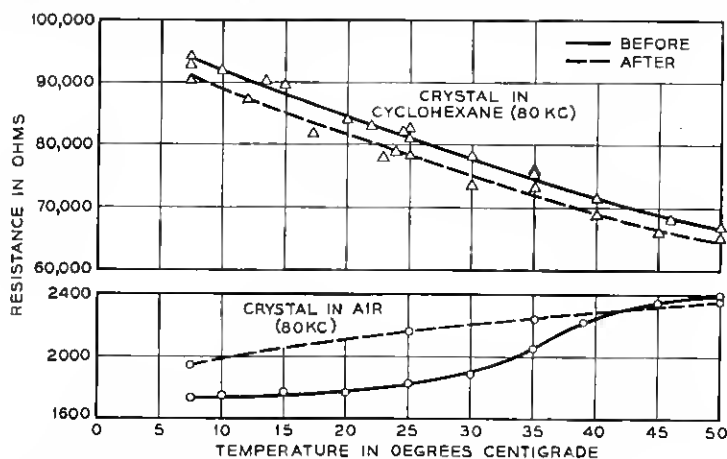


Fig. 11—Temperature variation of resistance at resonance before and after adding weights to mounting wires.

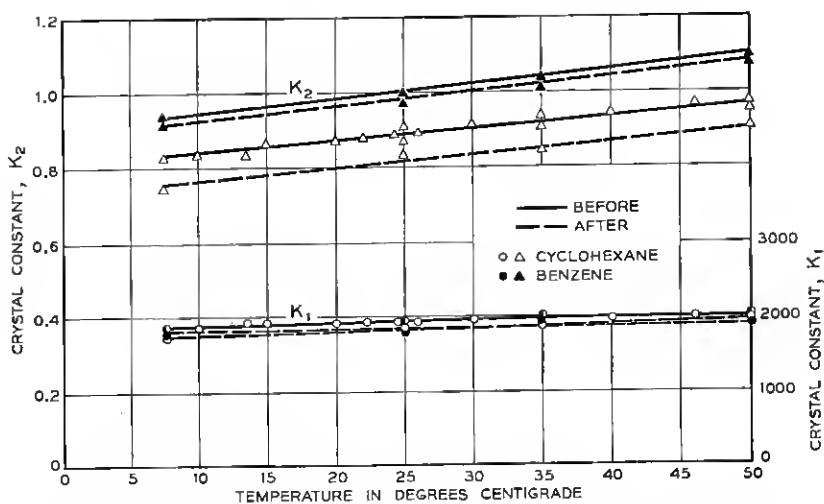


Fig. 12—Temperature variation of crystal constants  $K_1$  and  $K_2$  at 80 kc before and after adding weights to mounting wires.

harmonics. In this way, and in about 30 sec a balance can be conveniently achieved and the required ten-fold gain in accuracy attained.

By these means, and with best literature values of viscosity and density (which were checked in the laboratory at several temperatures) for purified solvents, curves for  $K_1$  and  $K_2$  were obtained as exhibited in Fig. 12 for 80 kc. Behaviour of  $K_1$  at different frequencies over a tem-

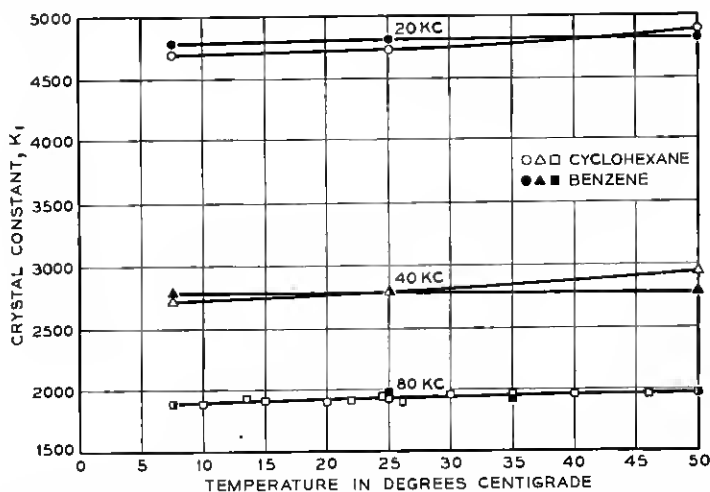


Fig. 13—Temperature variation of crystal constant  $K_1$  over a frequency range with benzene and cyclohexane as standard fluids.

perature range is shown in Fig. 13, and of  $K_2$ , in Fig. 14. Fig. 14 brings out the significant point that in the present arrangement, where the oscillating crystal is immersed in the liquid studied, the *dielectric* properties of the liquid are important. Apparently the dielectric losses even of these purified hydrocarbons are different enough so that  $K_2$  at 80 kc is quite different for benzene and cyclohexane. (Dielectric studies have previously indicated difficulty in preparing benzene having theoretically expected loss.) It is also possible that slight differences in wetting the crystal cause  $K_2$  to vary with the liquid used.

The  $K_1$  and  $K_2$  values determined for all the various conditions above were then used under these conditions for measurements on the polymer

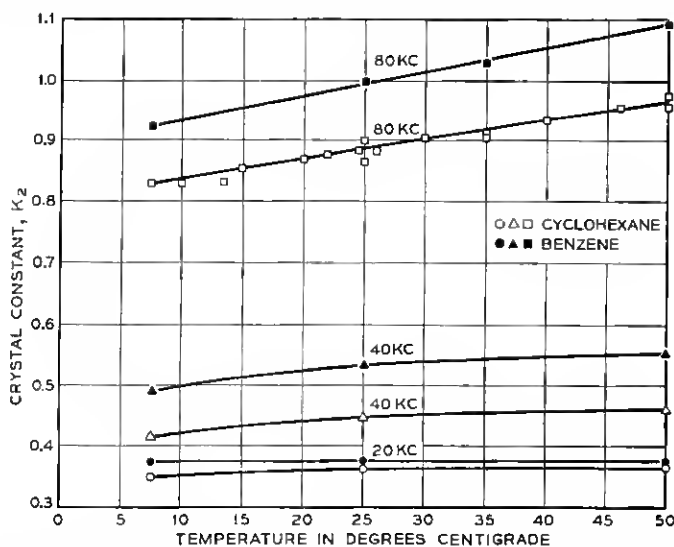


Fig. 14—Temperature variation of crystal constant  $K_2$  over a frequency range with benzene and cyclohexane as standard fluids.

solutions in the kilocycle range. In the megacycle range, the balanced shear wave reflectance technique<sup>23</sup> gave satisfactory results over certain concentration zones which could fairly well be extrapolated to high dilutions. Thus, over the whole spectrum, there seems to be no doubt about the reality of the effects described below. That is, their magnitude far exceeds experimental uncertainty, as demonstrated in this section.

#### POLYISOBUTYLENE SOLUTIONS; DYNAMICS OF SEPARATE CHAINS

Solutions of polyisobutylene of  $\bar{M}_n = 1.2 \times 10^6$  from about 0.1 to 1.0 wt. per cent concentration in cyclohexane yield  $R_M$  and  $X_M$  curves as shown in Fig. 15. The points coincide for the pure solvent, as they



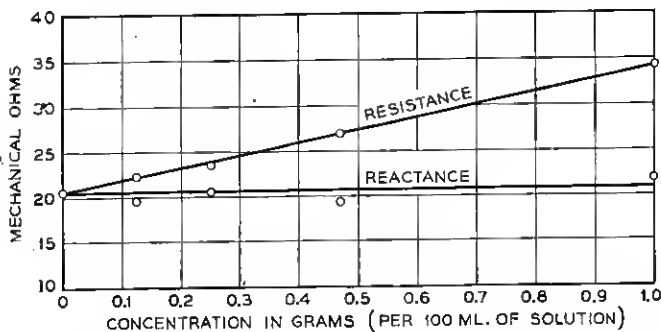


Fig. 15—Electromechanical interaction of solutions of polyisobutylene ( $\bar{M}_v = 1.18 \times 10^5$ ) in cyclohexane with crystal vibrating torsionally at 20 kc.

should for a liquid having only viscosity. But, apparently as soon as any polymer chains are added, the curves diverge. A stiffness coming from separate chain molecules is being displayed.<sup>50</sup> Qualitatively, theoretical expectations of Kuhn<sup>51, 52</sup> and others seem justified, at least that there is a relaxation mechanism for isolated chains.

The usual question of how best to express the dynamical results arises. The procedure of earlier sections for polymer solids and liquids will be followed. In general, a frequency dependent modified *Maxwell* element as sketched on Fig. 16 will be used. However, a frequency-independent analysis has also been carried out for one sample system, and, from this, basic mechanical constants of single "average" molecules are obtained, if it is reasonable to relate the mechanical models for the liquid continuum to the discrete chains dissolved in it.

Fig. 17 shows typical results from the simple scheme of Fig. 16, where the pure solvent viscosity,  $\eta_A$ , has been considered to be in parallel with a Maxwell element. The total shear rigidity of the solution (at a given concentration) is represented by  $\mu_B$ . The viscosity of the polymer molecule coils in solution with the solvent streaming through them is

$$\mu_B = \frac{(R^2 - X^2) \omega \eta_B}{\omega \rho \eta_s - 2RX}$$

$$\eta_A + \eta_B = \eta_s$$

$$\eta_A = \frac{2RX}{\omega \rho} - \frac{(R^2 - X^2)^2}{\omega \rho} \cdot \frac{1}{\omega \rho \eta_s - 2RX}$$

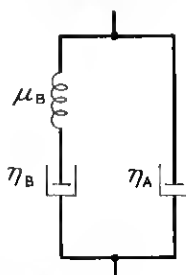


Fig. 16—Relations for calculation of shear stiffness and viscosity of dilute polymer solutions.

taken to be  $\eta_B$ . Thus, the steady flow viscosity,  $\eta_s = \eta_A + \eta_B$ . Also,

$$\frac{\eta_A + \eta_B}{\eta_A} = \eta_r \quad \text{or} \quad \frac{\eta_B}{\eta_A} = \eta_{sp}$$

under steady flow, or, alternatively, approximately a "dynamic intrinsic viscosity"

$$\left[ \frac{\eta_B}{\eta_A} \cdot \frac{1}{c} \right]_{c \rightarrow 0}$$

can be written for any given frequency.

The curves in Fig. 17 are frequency dependent, however, although it turns out that  $\eta_B$  is only slightly so. Nevertheless, the considerable rise of  $\eta_A$  above the pure solvent viscosity, as the concentration is increased, indicates other mechanisms are being lumped into  $\eta_A$ . As usual, some

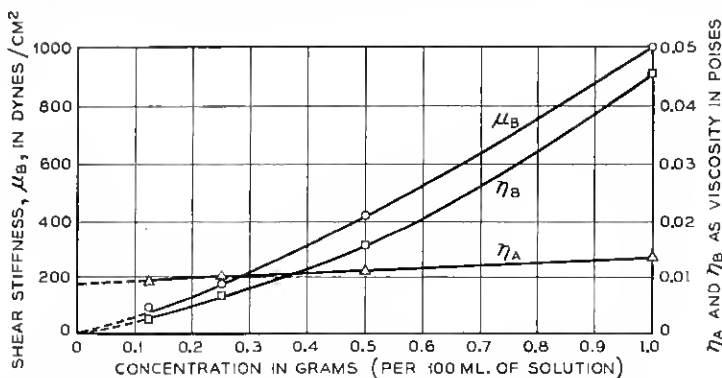


Fig. 17—Rigidity and viscosities of polyisobutylene ( $\bar{M}_v = 1.18 \times 10^6$ ) in cyclohexane, at 25°C and 20 kc.

extensive distribution of relaxation times is probably responsible. However, from the chemical point of view, it is best to see if some principal mechanisms related to known structures can be identified. If so, they could be associated with new ideas about the details of polymer intrinsic viscosities, as well as the form of isolated molecules.<sup>52, 53, 54, 55</sup>

First, the frequency dependence of the  $\mu_B$  of the model of Fig. 16 is as shown on Fig. 18. Striking regions of dispersion appear, although more points are needed to define the  $10^5$  cycle zone. Actually, many sets of data have been obtained in the  $10^4$  cycle zone. Recently, an immersed quartz tuning fork has given the approximate value shown for 2300 cycles. The experiments of Fig. 18 were on a polyisobutylene having  $\bar{M}_v = 3.9 \times 10^6$ , dissolved in cyclohexane. Values of  $\eta_A$  and  $\eta_B$  were, of course, also obtained. The results were then analyzed for a system of

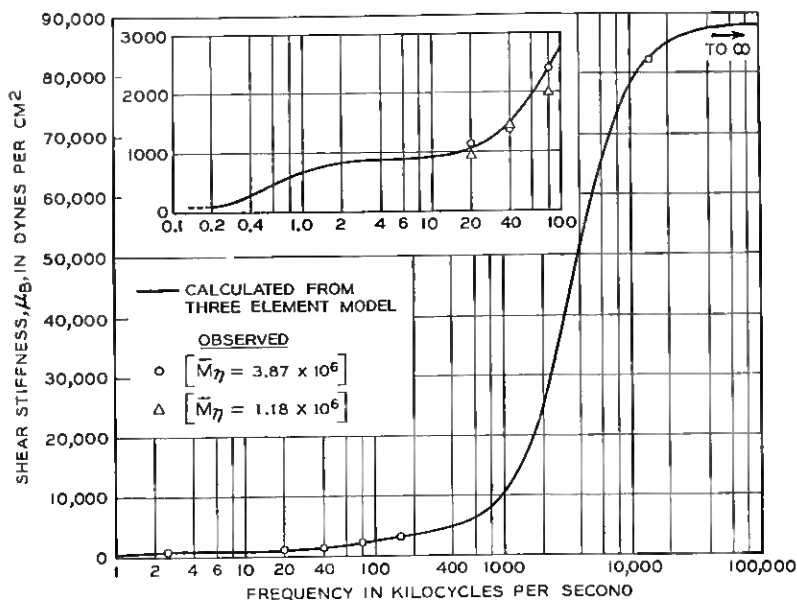


Fig. 18—Frequency dependence of shear stiffness of 1 per cent solutions of polyisobutylene in cyclohexane at 25°C.

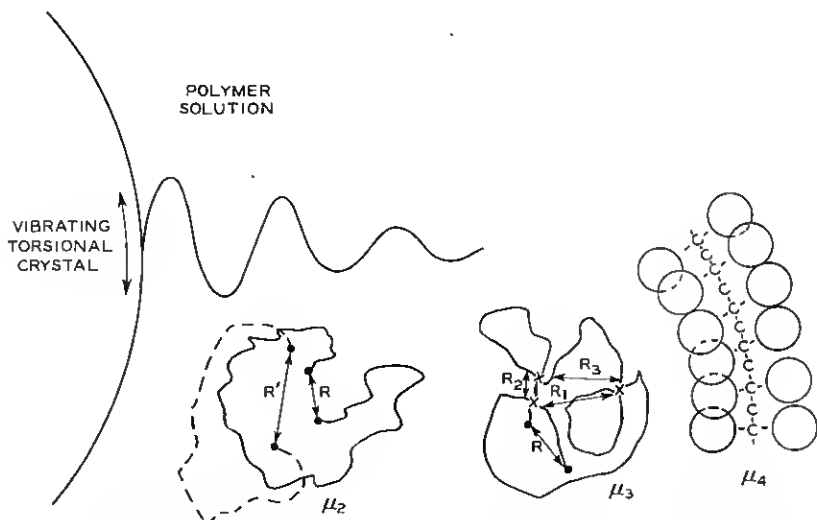


Fig. 19—Schematic diagram of possible sources of rigidity of single chain molecules in solution.

three Maxwell elements in parallel with again, as in Fig. 16, a solvent viscosity, this time called  $\eta_1$  (truly absolute solvent viscosity) in parallel with them. The  $\mu_R$  curve of Fig. 18, running through the observed points could then be calculated, by some special trial methods, with which Messrs. H. T. O'Neil and O. J. Zobel of Bell Telephone Laboratories kindly helped.

This analysis, identifying three principal relaxation regions for the motions of polyisobutylene chains in cyclohexane, gave for a 1 per cent solution (taken as linear part of concentration curve and hence equivalent to high dilution).

Principal rigidities  $\mu_2 = 890 \text{ dynes/cm}^2$

$\mu_3 = 3,190 \text{ dynes/cm}^2$

$\mu_4 = 84,000 \text{ dynes/cm}^2$

Principal viscosities  $\eta_1 = 0.0082 \text{ poise (pure cyclohexane)}$

$\eta_2 = 0.255 \text{ poise}$

$\eta_3 = 0.006 \text{ poise}$

$\eta_4 = 0.004 \text{ poise}$

Principal relaxation frequencies  $f_2 = 550 \text{ cycles}$

$f_3 = 8.45 \times 10^4 \text{ cycles}$

$f_4 = 3.52 \times 10^6 \text{ cycles}$

Tentatively, these mechanisms may be schematically described as on Fig. 19. Here, the polymer coil, subjected to shear waves in dilute solution, exhibits rigidities  $\mu_2$ ,  $\mu_3$  and  $\mu_4$ , all shown on different scales.  $\mu_2$  is the configurational elasticity because of actual changes in root mean square separation of chain ends, as from  $R$  to  $R'$ . It is retarded by viscous drag through the solvent,  $\eta_2$ , which is presumably the main source of characteristically high  $\eta_r$  of chain polymer solutions. The relaxation frequency for this mechanism is low—a few hundred cycles. It may come in significantly in work on more concentrated solutions at low frequencies,<sup>28, 45, 48, 57</sup> where chain entanglement is nevertheless the *dominant* factor.

$\mu_3$  is when segments of the same chain in the molecular coil temporarily entangle with each other. Striking evidence has recently been given by Fox and Flory<sup>58</sup> that because of mutual interference, the theoretical random flight configuration of a chain gives very much too small a

molecular coil volume,  $V_e$ . This suggests that thermal agitation tending toward a smaller  $V_e$ , and excluded volume or repulsions forcing a large one, will cause collisions or entanglements which might last long enough to give a *van der Waals* cross-bond as denoted by crosses on the  $\mu_3$  sketch. (The actual forces in these would somewhat resemble those between different molecules in the concentrated solutions of Ferry.<sup>28, 37</sup>) This mechanism has the reasonable (based on Ferry's and others' work) relaxation frequency of  $8.45 \times 10^4$ . A small viscosity,  $\eta_3$ , may comprise friction of slippage at the entanglement points, with both the polymer and associated solvent molecules.

In Fig. 19,  $\mu_4$  is a relatively high stiffness presumed to be some average hindrance to rotation of one segment with respect to another. In the sketch, close-packed spheres representing methyl groups in polyisobutylene are portrayed. Their force fields overlap more in some places than others, in the meandering of the chain to form the molecular coil (of course, some tail-to-tail structures may be important here; they have all been shown head-to-tail in the sketch). Thus, this total internal steric restraint on chain flexibility, with a relaxation frequency of  $3.5 \times 10^6$ , contributes greatly to the large dispersion of rigidity in the megacycle range noted in Fig. 18. The related viscosity,  $\eta_4$ , is again low.

There is no doubt a considerable distribution of relaxation characteristics associated with each and all of these mechanisms.

### *Physical Properties Per Molecule*

Since the viscosities and rigidities in the dilute solutions indeed seem to be additive with the number of molecules present, values of these properties, for the hypothetical mechanisms, can be expressed per average chain. Of course, the measured quantities are expressed as constants per cc of solution, but it may be useful to think of in terms of one average chain in each cc. Then, the shear deformation of this chain could be denoted by a force constant. The associated viscosities remain, however, dependent on solvent surroundings. Thus, for the polyisobutylene of  $\bar{M}_\eta = 3.9 \times 10^6$ , in cyclohexane solution, at 25°C the molecular quantities are:

$$\begin{array}{ll} [f_2] = 17 \times 10^{-13} \text{ dyne cm} & [\eta_2] = 1.6 \times 10^{-16} \text{ poise} \\ [f_3] = 6 \times 10^{-12} \text{ dyne cm} & [\eta_3] = 3.9 \times 10^{-18} \text{ poise} \\ [f_4] = 16 \times 10^{-11} \text{ dyne cm} & [\eta_4] = 2.4 \times 10^{-18} \text{ poise} \end{array}$$

In the section on polymer liquids, the high-frequency modulus  $\mu$  was attributed to a nearest-neighbor glass or crystal-like interaction (since the actual values were indeed typical of the hardest organic solids).

However, in polyisobutylene (and to some degree in poly- $\alpha$ -methyl styrene), it is especially difficult to distinguish *inter-chain* from *intra-chain* crowding of methyl groups. Thus, while average center-to-center separation of methyls is  $\sim 4 \text{ \AA}$  in adjacent chains,<sup>40</sup> it is  $< 2.5 \text{ \AA}$  within chains, in polyisobutylene. This crowding is apparently strouge; the observed  $\Delta H_{\text{pzn}}$  is only 12.8 kcal per mole instead of the 19.2 expected.<sup>55, 56</sup> The energy of steric hindrance thus amounts to almost half of the actual heat of polymerization. It is reasonable that a large part of the hardness of a mass of polyisobutylene chains, such as in the liquids, should therefore reflect the same mechanism as that for  $\mu_1$  (Fig. 19) in the dilute solutions. A rough check on this can be made. A polyisobutylene having considerably lower molecular weight than  $3.9 \times 10^6$  and thus intermediate between the "liquid" and "solid" ranges, had a Maxwell shear modulus in the megacycle region (14 mc) of  $\mu = 5.3 \times 10^9$ , at 25°C. The number of molecules/cc, with individual  $[f_1]$  given above, necessary to give the observed density of this polymer was multiplied by  $[f_1]$ , giving  $\mu = 2.8 \times 10^9$  dynes/cm<sup>2</sup>. Accordingly, about half of the observed high frequency rigidity of polyisobutylene, at 25°C, may be calculated from a "molecular constant" embodying intra-chain stiffness.

Much more refined and detailed treatments are required to generalize these "molecular constants" which are after all, as shown below, dependent on using a thermodynamically "inert" solvent. However, much as structurally significant dipole moments can be derived from measurements in dilute solutions, it seems hopeful that macromolecular mechanics can be so elucidated. Also additional structures, such as polypropylene and polydimethyl siloxane compared to polyisobutylene, are currently being studied.

### *Temperature Variation*

Some further behaviour at different temperatures and solubilities of separate chains in dilute solution may now be considered against this background of possible mechanisms. Practically, these studies will bear on processing and properties, lacquers, paints, and casting solutions of polymers, as well as on the other qualities outlined in the introduction. Results may be conveniently discussed in terms of the modified Maxwell single element, with factors  $\eta_A$ ,  $\eta_B$ , and  $\mu_B$  (Fig. 16). Mostly, the kilocycle range, reflecting molecular coil changes, will be of interest. For comparison, it may be noted that at 20 kc, the polyisobutylene whose  $\mu_B = 1061$  dynes/cm<sup>2</sup> in 1 per cent solution in cyclohexane receives 889 dynes/cm<sup>2</sup> of this from  $\mu_2$ , the retarded configurational mechanism; 169

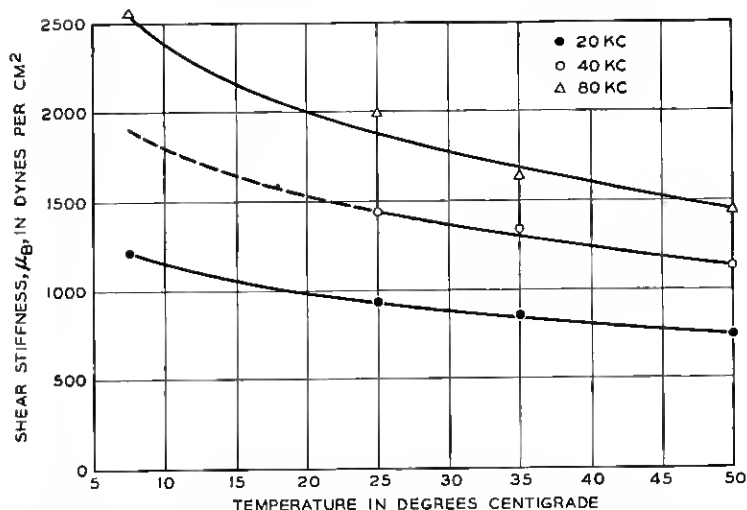


Fig. 20—Temperature variation of rigidity of 1 per cent solution of polyisobutylene ( $\bar{M}_n = 1.18 \times 10^6$ ) in cyclohexane.

dynes/cm<sup>2</sup> from the entangled segments stiffness,  $\mu_3$ ; and only 3 dynes/cm<sup>2</sup> from the intra-chain stiffness,  $\mu_4$ . Thus, chain configuration mechanics, including the associated viscosities, can be well enough thought of in the following paragraphs, in terms of  $\mu_B$ ,  $\eta_B$  and  $\eta_A$ .

The exponential decrease of  $\mu$  with temperature familiar for polymer solids and liquids is much suppressed in the  $\mu_B$  vs  $T$  curve of Fig. 20. While the  $\mu_4$ , internal rotation, mechanism for single polyisobutylene molecules probably has a considerable activation energy, that for the  $\mu_2$ , configurational, rigidity should be very small. Then, without retardation, the intrinsic chain modulus would rise with rising temperature. These influences seem to combine to give the modest decline of  $\mu_B$  appearing in Fig. 20. If these rigidities are plotted against  $1/T$ , the temperature coefficient is 2.3 kcal. This is much less than the familiar values for the stiffening of rubbery solids, and emphasizes that *inter-chain* action reigns then.

### Solvent Variation

Effects of solvents of different (mostly positive) heats of mixing on state of polyisobutylene molecules in solution have been nicely established by Fox and Flory.<sup>58</sup> Especially, this work has clarified principal factors in the intrinsic viscosity expression

$$[\eta] = \frac{V_e}{\bar{M}} \cdot \frac{\phi}{100} = K_0 M^{1/2} \alpha^3 \phi.$$

Here,  $V_e$  = effective volume per molecule (and hence as determined by chain configuration),  $M$  = molecular weight,  $\alpha$  represents change in linear extent of molecule because of mutual interference of segments<sup>58</sup> and  $\phi$  expresses the hydrodynamics interaction of solvent and molecular coil (including varying degrees of "straining through" the coil).<sup>61, 62, 63, 64</sup> Interpretation of the mechanical properties of chains in dilute solution, with reference to the rough concepts of Fig. 16, arouses particular interest in the factor  $\alpha^3$ . For a high molecular weight polyisobutylene, intrinsic viscosity theory<sup>58</sup> indicated that  $\alpha^3$  the ratio for volume of actual coil divided by volume for ideal random flight coil was 3.81 in cyclohexane but only 1.42 in benzene, both at 30°C. This striking alteration in equilibrium chain configuration, a variable which is not readily introduced into polymer liquids or solids, appears in the inherent viscosity vs  $c$  curves in cyclohexane, Fig. 21, and benzene, Fig. 22. The large difference in  $[\eta]$  at 25°C, 6.00 in cyclohexane vs  $\sim 1.5$  in benzene, indeed emphasizes the different solvent powers.<sup>65</sup> Likewise, the large increase of  $[\eta]$  with temperature in Fig. 22 accents the poor solvent qualities of benzene.<sup>66</sup> Too, empirically, polymer molecules which are either tight coils or are actually chemically cross-linked to form microgel molecules characteristically show *positive* slopes of inherent viscosity vs  $c$  plots.<sup>67</sup> Accordingly, all this evidence for large changes in the conformation of chain molecules in "good" vs "poor" solvents should show up in dynamics of dilute solutions. Also, technically, quite different physical properties are found for polymer-plasticizer compounds where compatibility is high (good solvent) than where it is low (poor solvent). Here,

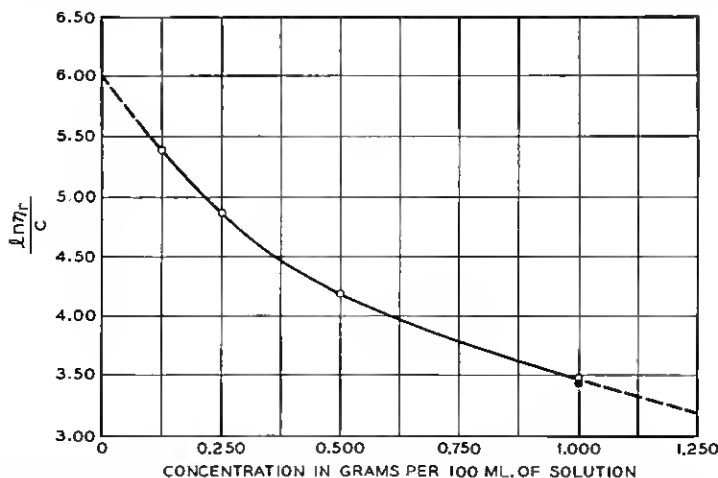


Fig. 21—Inherent viscosity of polyisobutylene ( $\bar{M}_\eta = 3.87 \times 10^6$ ) in cyclohexane at 25°C.



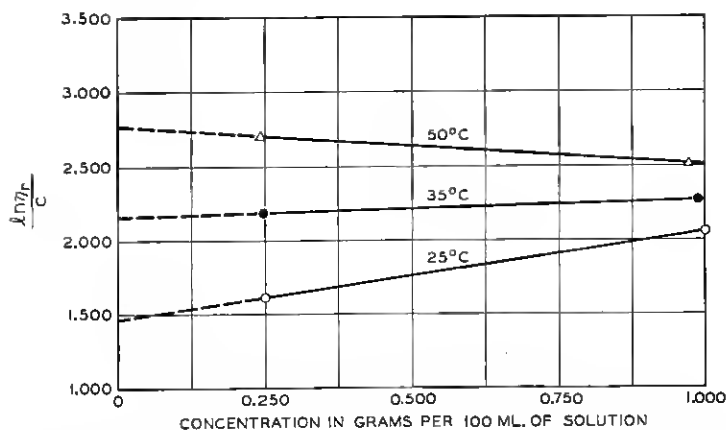


Fig. 22—Inherent viscosity of polyisobutylene ( $\bar{M}_\eta = 3.87 \times 10^6$ ) in benzene, at various temperatures.

more flexible compositions are often produced with low compatibility plasticizers—indeed, sometimes with those on the verge of phase separation than with those with highly favorable heats of solution.<sup>68</sup> This would mean that the bad solvents would compress the chains so that they would be more easily strained than if they were in a “free chain” or even extended configuration. If single chain, visco-elastic stiffnesses are acting this way, the dynamic  $\mu_B$  would then actually decline as heat of mixing become more positive.

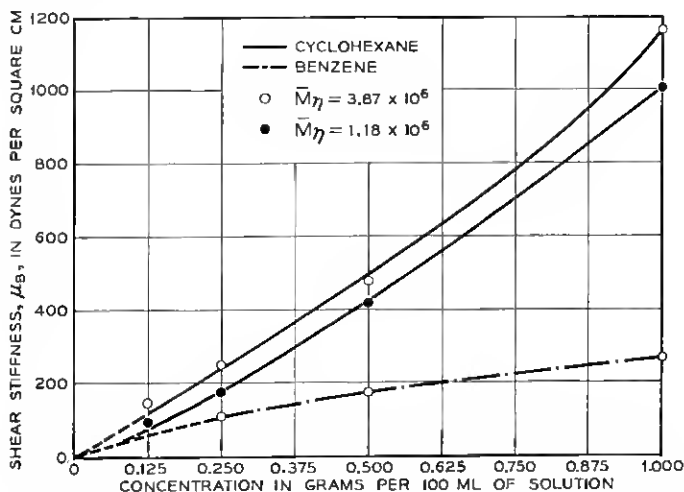


Fig. 23—Rigidity of polyisobutylenes in cyclohexane and benzene at 25°C and 20 kc.

This seems to take place, as indicated by the lower compared to the upper curve on Fig. 23. Here, the  $\mu_B$  of the usual modified Maxwell model, at 20 kc, is plotted against  $c$  for the polyisobutylene of  $\bar{M}_v = 3.9 \times 10^6$ . Also, the middle curve shows  $\mu_B$  for a polymer of about a third of this molecular weight; while there is a small reduction in  $\mu_B$  with  $\bar{M}_v$  in this range, it is much less than the reduction caused by tightening up the polymer coil.

The  $\mu_B$  values per average molecule,  $[f_B]$ , fall from  $18 \times 10^{-13}$  dyne cm in cyclohexane to  $7 \times 10^{-13}$  in benzene. (Of course,  $[f_B]$  for the intermediate molecular weight polymer in cyclohexane is only  $5 \times 10^{-13}$  because so many more molecules are present in solution.)

The temperature dependence of  $\mu_B$  also becomes nearly zero at least over the narrow range from 25 to 50°C, in benzene compared to cyclohexane. This seems to accord with the indications previously, from Fig. 20, for a lower molecular weight polymer, that different mechanisms are competing. These may be the configurational, with  $\mu \propto T$ , and relaxation, with  $\mu$  varying in some complicated way with  $T$ . Thus  $[\eta]$  increases markedly with  $T$ , and presumably denotes an expanding molecular coil tending toward the "normal" configuration in cyclohexane. At the same time, the relaxation processes with rising temperature tend to cause the decrease in  $\mu_B$  typical of the upper, solid, curves on Fig. 24. In engineering use, often times poorly compatible plasticizers give compounds which stiffen more gradually with temperature than do "solvent" plasticized ones.

For similar reasons, the dynamic molecular coil viscosity,  $\eta_B$ , ought to vary less with temperature in thermodynamically poor than in good solvents. This is indeed seen in Fig. 25. On the other hand,  $\eta_A$  for the modified Maxwell element has been described as the solvent viscosity with segment hindrance and restricted rotation terms from the polymer molecules lumped in with it. These latter terms are presumably little affected by over-all configuration ( $\mu_2$  term; the  $\mu_3$  mechanism will be somewhat affected, but not the  $\mu_4$ , on Fig. 19). Thus,  $\eta_A$  should have comparable temperature dependence in both good and bad solvents, as seems to be indicated by Fig. 26.

### *Microgel Molecule Solutions*

The statistical coil of linear polymer molecules may be replaced by a chemically fixed, cross-linked network in microgel molecules.<sup>67</sup> These may be made completely rigid, like Einstein spheres, or highly swellable. The latter are hybrids between rigid spheres and coiled chains. In

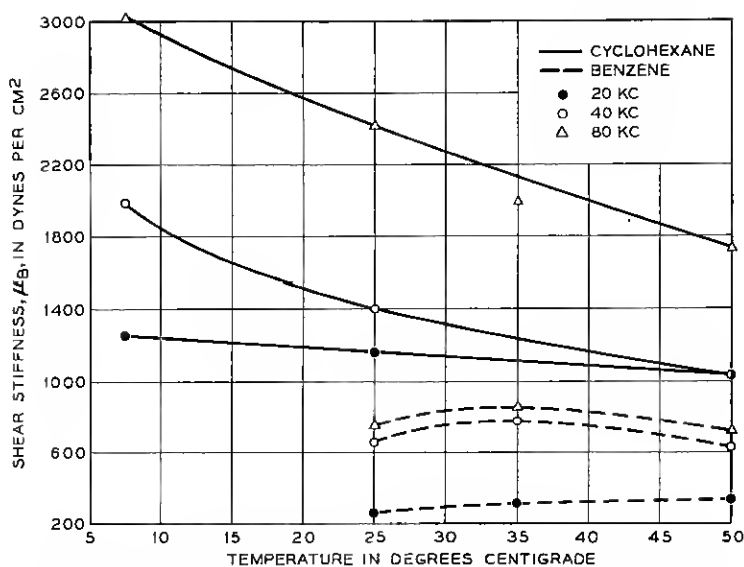


Fig. 24—Temperature variation of rigidity of 1 per cent solution of polyisobutylene ( $\bar{M}_\eta = 3.87 \times 10^6$ ) in cyclohexane and benzene.

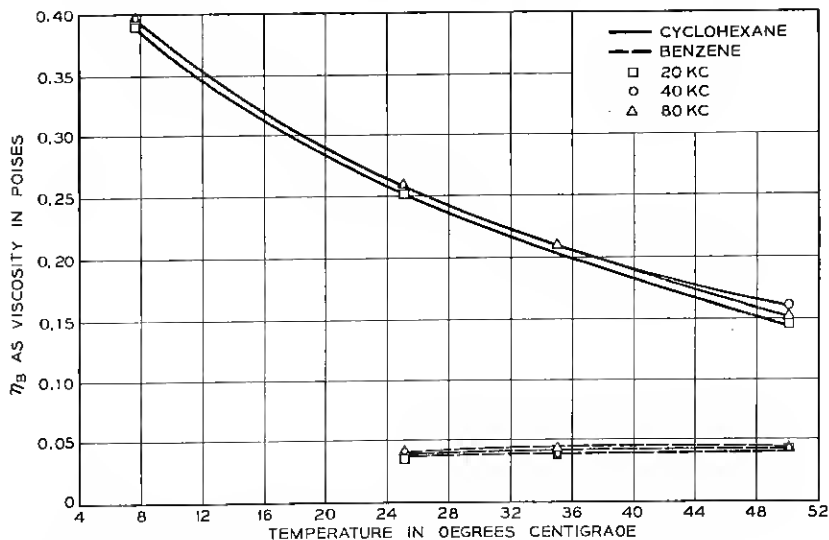


Fig. 25—Temperature variation of  $\eta_B$  for 1 per cent solution of polyisobutylene ( $\bar{M}_\eta = 3.87 \times 10^6$ ) in cyclohexane and benzene.

synthetic rubber, they confer unique flow properties, causing the excellent processibility of GR-S 60. However, dynamic tenacity, such as in flex crack growth, is degraded by their presence. Now presumably the excellent extrusion qualities of synthetic rubber composed of from 60 to 80 per cent microgel molecules are because of their individual shear stiffness. Thus, if a wire coating, for instance, is extruded at high rates of shear, chain molecules are deformed, and store energy just as discussed in the earlier sections on liquids. After emerging from the extrusion die, they relax, and cause the gross retraction, shrinkage and roughness shown in the wire insulation of the upper photograph of Fig. 27. A polymer with about 70 per cent microgel molecules gives the smooth covering shown in the lower specimen of Fig. 27. Here, the shearing stresses of extrusion seem insufficient to distort the tiny networks of the microgel molecule; in any case, the covering does not roughen or relax. Similar effects have been found for microgel plastics. Nevertheless, unlike gross or macro gelation, the whole melt can flow.

On this basis, dilute solutions of microgel molecules ought to indicate high shear rigidity per molecule. The mechanism  $\mu_3$  of Fig. 19, in which now the junction points are not temporary, but are primary valence cross-links, should be predominant. Fig. 28 shows, for a polybutadiene microgel in cyclohexane,<sup>67</sup> that  $\mu_B$  has indeed risen, compared to equal

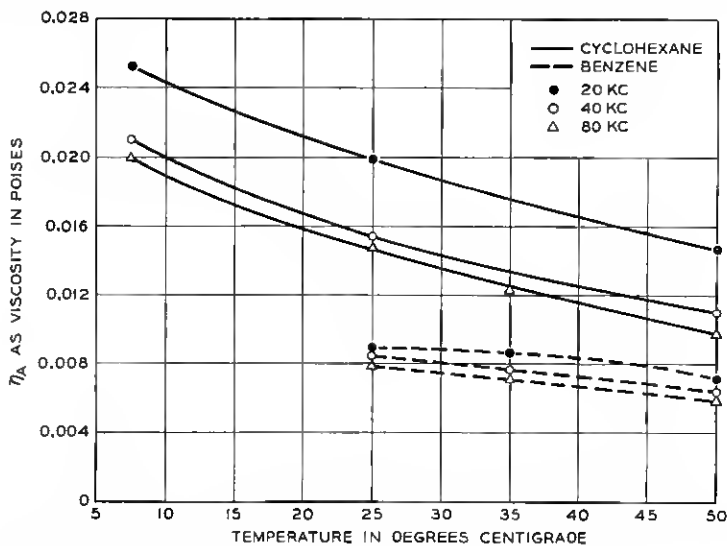


Fig. 26—Temperature variation of  $\eta_A$  for 1 per cent solution of polyisobutylene ( $\bar{M}_v = 3.87 \times 10^6$ ) in cyclohexane and benzene.



Fig. 27—Effect of microgel molecules in synthetic rubber on smoothness of extruded wire insulation. Rough covering is from high-speed extrusion of GR-S without microgel.

weights of chain molecules. Further, accompanying the extremely high average molecular weight of the microgel ( $18.6 \times 10^6$ ), the  $[f_B]$  per average molecule is  $42 \times 10^{-12}$  dyne cm or about twenty-five times that of the polyisobutylene with  $\bar{M}_v = 3.9 \times 10^6$ . Also, the temperature coefficient for  $\mu_B$  of polybutadiene microgel is low.

Of course, polybutadiene, as chains or as microgel molecule segments, has many double bonds. These will surely influence the  $\mu_4$ , or internal rotation mechanism. Further work remains to show just what is their effect in the microgel case. But, it is interesting to compare  $\mu_B$  values for Hevea rubber chains with those for, say, polyisobutylene, which has only single bonds in the chain.

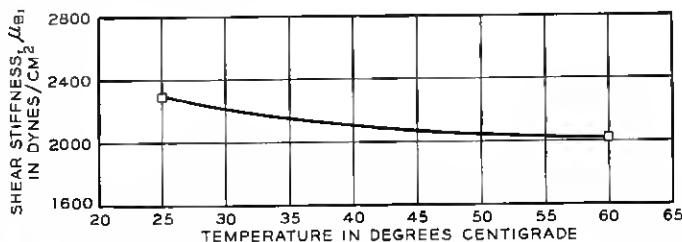


Fig. 28—Rigidity of 0.5 per cent solution in cyclohexane of polybutadiene microgel ( $\bar{M}_w = 18.6 \times 10^6$ ) at 20kc.

*Hevea Rubber Solutions*

The comparison of equal weight concentrations of natural rubber in cyclohexane with polyisobutylene in cyclohexane is surprising:

Hevea rubber  $\bar{M}_\eta = .23 \times 10^6 \mu_B = 1350 \text{ dynes/cm}^2$ , 1 per cent solution (corr.).

Polyisobutylene  $\bar{M}_\eta = 1.2 \times 10^6 \mu_B = 1000 \text{ dynes/cm}^2$ , 1 per cent solution (corr.).

Both results are at 20 kc. The higher value for natural rubber may be because of the double bonds causing stiffening of the chain. On the other hand, maybe easy rotation around single bonds raises the  $\mu_3$  part. Certainly the *viscous* retardation *within* natural rubber chains is very low, as noted in the section on solids. However, its interaction with, or configuration, in cyclohexane may be peculiar. The  $[f_B]$  per average molecule is, however, low, being  $15 \times 10^{-14}$  dyne cm at 25°C.

*Polystyrene Solutions*

Much work, on light scattering and other properties, has indicated appreciable intra-chain stiffness for polystyrene,<sup>69</sup> but still much freedom compared to polyisobutylene.<sup>69a</sup> However, this work, as well as  $\Delta H_{pzn}$  of 17 kcal compared to  $\sim 49$  kcal calculated for no steric hindrance, suggests comparatively small restraints on ideal flexibility. This needs to be checked by a frequency analysis of dilute solution mechanics, but polystyrene seems to be a reasonable example of "plastic" behaviour at room temperature because of interaction *between* the chains. (It is recalled that, earlier,  $\alpha$ -methyl styrene polymer was cited as plastic model showing both intra- and inter-chain stiffness. Unlike in polystyrene, the intra-chain factor shows up in a  $\Delta H_{pzn}$  of 9–10 kcal, a third less than that calculated if there were no steric hindrance.) Thus, no evidence of unusual stiffness appears in Fig. 29, when, indeed, the  $\mu_B$  values are considerably lower, for equal weight concentrations, than those for natural rubber. The highly milled rubber studied had  $\bar{M}_\eta$  very nearly that of  $\bar{M}_\eta = 0.234 \times 10^6$  of the polystyrene, so the  $[f_B]$  per average polystyrene chain,  $4.5 \times 10^{-14}$  dyne cm is less than a third that of the rubber. No wonder that at high temperatures, where the phenyl group interaction between chains is much reduced, polystyrene makes a good rubber. Also, in Fig. 29 are shown data for a polymer of  $\bar{M}_\eta = 1.2 \times 10^6$ , made in emulsion and having  $[\eta] = 4.350$  in benzene at 25°C.

The polystyrene solutions discussed above were in benzene, a good solvent. Here, the situation is converse to that for polyisobutylene; for polystyrene, cyclohexane is a poor solvent and benzene, good. Hence, if the previous interpretation of reduced single chain *quasi-configurational* ( $\mu_2$ ) stiffness is general for solvents of more endothermic mixing, the "plastic" molecule polystyrene should show it in cyclohexane. This is indeed evident in Fig. 30, showing one of the same polystyrenes of Fig. 29, measured at 20 kc (normalized to 1 per cent concentration). Also, on Fig. 30 are shown the inherent viscosity (practically, the intrinsic viscosity, in this case) and the absolute viscosity of the 1 per cent solution

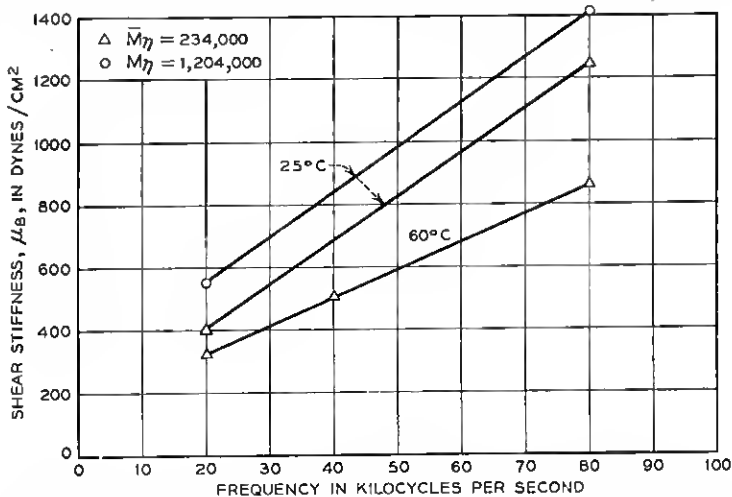


Fig. 29—Change of shear stiffness,  $\mu_B$ , with frequency, for 1 per cent solutions of polystyrene in benzene.

under steady flow,  $\eta_s$ . These are all plotted against temperature down to phase separation, at about 26° to 27°C.

The marked positive slope of the  $\ln \eta_r/c$  curve denotes the large contraction in molecular coil volume preceding phase separation or insolubility. The absolute viscosity,  $\eta_s$ , however, rises with declining temperature because it is dominated by solvent viscosity, but when the polymer phase comes out,  $\eta_s$  abruptly falls off.

The  $\mu_B$  values are consistent with this steady flow behaviour, except that the rise of  $\mu_B$  at the turbidity point seems to be because a layer of swollen polymer-rich phase forms on the torsional crystal surface. This condition is seen in Fig. 30 to coincide nicely with the abrupt changes in steady flow viscosity.

The slight maximum in the  $\mu_B$  curve at about 35°C may not be real.

It does come near the point of minimum interaction for the whole system. In any case, as discussed before, the average temperature coefficient of  $\mu_B$  in the poor solvent is very low compared to the good solvent. The values of  $\mu_B$  are roughly  $\frac{2}{3}$  to  $\frac{1}{2}$  those in benzene.

#### GENERAL THEORY OF SINGLE CHAIN MECHANICS; KUHN AND KIRKWOOD

As noted before, much of the present understanding of stress-strain properties of polymer chains, in dilute solutions, liquids or solids, has come from W. Kuhn's long interest in this subject. Many supplementary contributions have been stimulated by Kuhn's work, and new points of view have been introduced by others. For instance, recently new and different proposals have been made about the flow birefringence and non-Newtonian viscosity of solutions of deformable spheres.<sup>70</sup> These ideas could be tested on suitable microgel solutions.

Recently, moreover, an especially significant general theory of viscoelastic behaviour of polymer in solution has been constructed by Kirkwood.<sup>71</sup> It explicitly considers the hydrodynamic conditions leading to the rigidity now observed for high-frequency shear waves. It formulates definitely the configurational changes of isolated chains in solution when strained in shear. As this theory is advanced to forms where simpler calculations can be made, it may answer many of the questions raised by the new experiments on single chain properties.

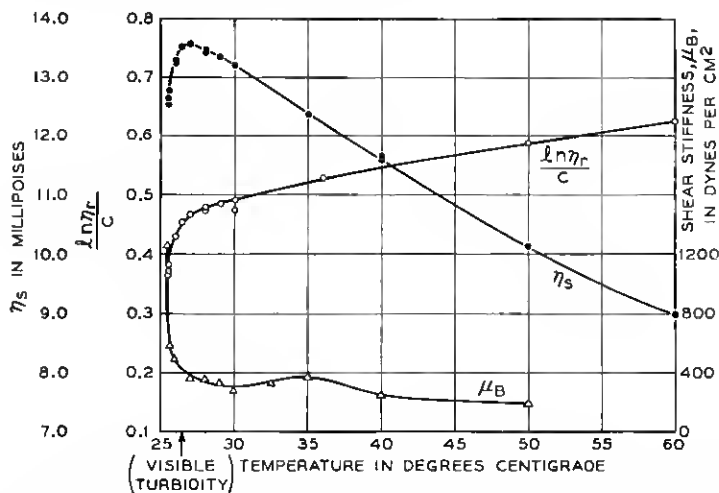


Fig. 30—Temperature dependence of absolute viscosity,  $\eta_s$ , inherent viscosity,  $\ln \eta_r / c$ , and shear stiffness,  $\mu_B$ , of, 1 per cent solution of polystyrene in cyclohexane down through turbidity point.



## CONCLUSIONS

To leave some impression of the elemental chemical structures which move around when wood, rubber, plastics, textiles and finishes are used mechanically—that has been the aim of this study. Polymer viscosities have been found in a variety of “solids”; rigidities have been demonstrated for very fluid “liquids” and solutions. Studies of these solid and liquid extremes have given some chemical reality to the classical spring and dashpot models.

Existence of compressional viscosity has been shown for polymer liquids and solids. It may comprise a new quality for investigation of polymer structure. At present, too little is known of its origin to interpret further the effects of intense ultrasonic irradiation of polymer solutions. Experiments of Schmid and co-workers<sup>72</sup> early indicated degradation of molecular weight of polystyrene, so irradiated, but whether this is chemical, from local heating in the solvent, or actual physical coupling with the wave field, is still unsettled. However, these workers also considered a compressional stiffness of the polymer molecules in the solutions,<sup>73</sup> and showed that if there was coupling, it was not inertial (by dissolving polystyrene in solvents of exactly the same density, no reduction in effect was observed). A point of general interest arises here; impact fractures of plastics presumably actually fracture some primary valence bonds. This is certainly true for many thermoset materials, and probably for chain compounds. Hence, if the detailed mechanism of how compressional waves move and perhaps rupture polymer segments were known, information on the baffling problems of ultimate strength would be gained. The observations above on dependence of  $\lambda$  and  $\lambda'$  on molecular weight and structure provide only the barest start on this but a new goal is in view. Too, basic questions of how rapidly molecules being formed in a polymerization equilibrate in temperature with their surroundings are elucidated by compressional wave propagation constants. For instance, absolute rate measurements on velocity of chain growth cannot be said to be isothermal if they seem to be faster than the thermal relaxation times which the ultrasonic measurements indicate can be  $\sim 10^{-6}$  to  $10^{-5}$  sec.

Likewise, more thorough understanding of velocity and dispersion of compressional waves in polymer solutions would clear up anomalies in velocity measurements for a wide variety of polymers,<sup>74</sup> some of which have been tentatively attributed to chain branching.

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